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REGISTERED NO. M. 3121

PROCEEDINGS

OF THE

INDIAN ACADEMY

OF SCIENCES

VOL. XI] *SECTION A* [NO. 1

JANUARY, 1940

Price Rs. 2 or 3 Sh. *Annual Subscription Rs. 18*

PRINTED AT THE BANGALORE PRESS, BANGALORE CITY, BY G. SRINIVASA RAO,
SUPERINTENDENT, AND PUBLISHED BY THE INDIAN ACADEMY OF SCIENCES,
HEBBAL, BANGALORE.

Physical
Ind.
Indian academy
10-15-43
#7604
v. 11, no. 1-6

INTENSITY OF RAMAN LINES IN CARBON TETRACHLORIDE

By B. Poornachandra Rao

(From the Department of Physics, Andhra University, Waltair)

Received December 9, 1939
(Communicated by Prof. S. Bhagavantam)

1. *Introduction*

Following Silberstein's explanation of the optical anisotropy of molecules, Ramanathan[1] amongst others utilised the observed depolarization factors to calculate the interatomic distances in some typical cases. These results are not in agreement with the values obtained from band spectra. Havelock[2] on the other hand, assumed the known interatomic distances and calculated the polarizabilities of the constituent atoms. This subject has now acquired a fresh importance since such calculations may be extended to the determination of the intensity of Raman lines. It is well known that the intensity of a Raman line depends upon the variation of the induced optical moment of the molecule with respect to the corresponding normal co-ordinate. Since the polarizability of a molecule can be determined from the above calculations, its dependence on a particular normal co-ordinate and hence the intensity of the corresponding Raman line may also be evaluated. In the present investigation, this method has been applied to the special case of the total symmetric Raman line in CCl_4. Some experimental results obtained by the author are compared with the theory.

2. *Expressions for a Tetrahedral Molecule*

Carbon tetrachloride has to be regarded as a regular tetrahedron with the four like atoms at its corners and the carbon atom at its centre. Havelock obtained the expressions for the polarizability of such a structure. This arrangement is optically isotropic and we have

$$\alpha = \frac{216\left(4+\frac{2a_1}{d^3}\right)a_1+a_2\left\{216+\frac{108a_1}{d^3}-\frac{(33011-2304\sqrt{6})^2\ 4a_1}{d^6}\right\}}{27\left(8+\frac{4a_1}{d^3}-\frac{36a_1}{d^6}\right)^2-\frac{8192\times 4a_1a_2}{d^6}} \cdot \quad (1)$$

In the above expression a_1 and a_2 are respectively the polarizabilities of the chlorine and the carbon atoms. d is the edge of the tetrahedron and α is the polarizability of the CCl_4 molecule. This expression can be simplified

to give (2) if we assume that the polarizability of the carbon atom is negligible. Such an assumption is only approximate and is justifiable if we regard that the carbon in this case is nearly in the form of an ion C^{4+}.

$$\alpha = \frac{4a_1 + 2a_1^2/d^3}{1 + \frac{a_1}{2d^3} - \frac{9a_1^2}{2d^6}}. \tag{2}$$

A simple relation given by $r = \frac{1}{4} d\sqrt{6}$ exists between the edge d of the tetrahedron and its radius r. The value of α can now be thrown into another form given below in (3).

$$\alpha = \frac{4a_1 + \frac{3\sqrt{6}\, a_1^2}{16r^3}}{1 + \frac{3\sqrt{6}\, a_1}{64r^3} - \frac{243\, a_1^2}{1024\, r^6}}. \tag{3}$$

The variation of the polarizability with respect to the total symmetric normal co-ordinate is obtained by differentiating (3) with respect to r as follows :

$$\frac{d\alpha}{dr} = \frac{\left(4a_1 + \frac{3\sqrt{6}\, a_1^2}{16\, r^3}\right)\left(\frac{9\sqrt{6}\, a_1}{64\, r^4} - \frac{243 \times 6\, a_1^2}{1024\, r^7}\right)}{\left(1 + \frac{3\sqrt{6}\, a_1}{64\, r^3} - \frac{243\, a_1^2}{1024\, r^6}\right)^2}$$

$$- \frac{9\sqrt{6}\, a_1^2}{16\, r^4\left(1 + \frac{3\sqrt{6}\, a_1}{64\, r^3} - \frac{243\, a_1^2}{1024\, r^6}\right)}. \tag{4}$$

The ratio of the intensity of the Raman line corresponding to the total symmetric oscillation of the tetrahedron to the Rayleigh line is given by the expression (5)

$$\frac{\text{I (Raman)}}{\text{I (Rayleigh)}} = \frac{h}{8\pi^2 \nu \mu} \frac{\left(\frac{d\alpha}{dr}\right)^2}{\alpha^2}. \tag{5}$$

μ stands for $m/4$ in this case where m is the mass of the chlorine atom. ν is the vibrational frequency of the corresponding Raman line.

So far, these calculations apply to the case of gaseous CCl_4 only. But the moment we go to the liquids state, complications set in. We have to introduce the compressibility of the liquid and the expressions have accordingly to be altered. Rayleigh scattering being coherent is reduced in the liquid in the ratio of $1 : \frac{RT\beta\nu}{N}$, where R is the gas constant, T is the absolute temperature, β is the isothermal compressibility, ν is the number of molecules per unit volume and N is the Avogadro number. The intensity of Raman

scattering remains unaltered as it is incoherent. The correction term can also be written as $\frac{R\,T\,\beta\,\rho}{M}$ where ρ is the density of the liquid and M is the molecular weight. Thus the ratio of the intensity of the total symmetric Raman line to the Rayleigh scattering in liquid CCl_4 may be calculated with the help of (5). The results are given in Table I.

3. Experimental Details and Results

The following technique is adopted for measuring the intensities of Raman lines. A step-filter over which a set of graded intensity steps are present is placed in the path of the scattered beam. The steps are in the ratio of 100 : 43 : 18·6 : 2·2 : 0·8. All the steps are clearly focussed on the slit of the spectrograph by means of a lens. Adjustments are so made that the upper and the lower portions of the image on the slit of the spectrograph are of uniform illumination. Carefully distilled CCl_4 is poured into the Raman tube and the condenser method of illumination is employed. " Selochrome " plates for which the photographic sensitivity over the region $\lambda 4046 - \lambda 4358$ has been determined by a prior experiment have been used. In about 24 hours, all the Raman lines are clearly recorded. The plate is run through a Moll microphotometer and the ratio of the peak intensity of the principal Raman line to that of the corresponding Rayleigh line is determined in the usual manner. The results are given in Table I.

TABLE I

Total Symmetric Raman Line in CCl_4

$r \times 10^8$	$a_1 \times 10^{24}$	a_2	$\frac{da}{dr} \times 10^{16}$	$a \times 10^{24}$		$\frac{I\,(Raman)}{I\,(Rayleigh)} \times 10^3$	
				calc.	obs.	calc.	obs.
1·755	2·43	0	1·63	10·2	10·4	3·6	2·0

The radius of the tetrahedron is obtaind from electron diffraction experiments.[3] a_1 refers to chlorine and this value is the same as that which has to be ascribed to chlorine in HCl in order to account for its refractivity and anisotropy. The observed value of 10·4 for a (CCl_4) is based on the value of $35{\cdot}39 \times 10^{-4}$ given by Havelock for $n^2 - 1$ for the D-line for CCl_4 vapour. The agreement between the calculated and observed values is satisfactory. The overtone of the 780 doublet in CCl_4 has also been recorded and an estimate is made of its intensity and state of polarization. These results are given in Table II.

TABLE II

780 *Doublet and the Corresponding Overtone in* CCl_4

Raman line	780 Doublet	1538 Overtone
Depolarization ..	·89	·41
Relative Intensities ..	7·7	1

Results obtained by the author are compared with those of the earlier investigators in Table III.

TABLE III

Intensity of Raman Lines in CCl_4

Line	I (Raman)/I (Rayleigh) $\times 10^3$		
	Daure	Veerabhadra Rao	Author
459	6	2·5	2·0
315	13	3·6	1·8
217	10	3·0	1·6

4. *Discussion of Results*

Veerabhadra Rao[4] and Daure[5] and others determined the intensities of the Raman lines and their results are at variance amongst themselves. The values obtained by the present author are of the same order of magnitude as those obtained by Veerabhadra Rao. The experimentally observed value of $2\cdot0 \times 10^{-3}$ for the intensity of the principal Raman line in CCl_4 may be compared with the theoreticl estimate, namely $3\cdot6 \times 10^{-3}$ given in Table I. The agreement is satisfactory. The fact that the overtone at 1538 exhibits partial polarization while the corresponding fundamental is depolarized to the limit is an interesting result. That we should expect such a situation has recently been shown by Bhagavantam and Venkatarayudu.[6]

5. *Summary*

Assuming a tetrahedral structure for CCl_4, its mean polarizability and the intensity of the Raman line corresponding to the total symmetric expansion have been calculated and compared with the experimentally observed values. The agreement is satisfactory.

The first overtone of the Raman doublet at about 780 has been recorded and its state of polarization studied. The fact that it has been found to be well polarized, although the fundamental is depolarized to the limit, is in agreement with what may be expected on theoretical grounds. The total intensity of the fundamental has been found to be about 8 times as much as that of the overtone.

In conclusion, the author desires to express his grateful thanks to Prof. S. Bhagavantam for the keen interest he has shown during the progress of this work.

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ON m CONSECUTIVE INTEGERS—I*

By S. S. Pillai

(From the Department of Mathematics, Annamalai University)

Received December 12, 1939
(Communicated by Prof. B. S. Madhava Rao)

I

The object of this paper is to prove the following :

Theorem I : *When* m $\leqslant$ 16, *in every set of* m *consecutive integers, there is at least one integer which is prime to all the rest in the set.*

When $m = 17$, below 30030 ($= 2, 3, 5, 7, 11, 13$) there are two sets of 17 consecutive integers which do not satisfy the condition of theorem. They are 2184——2210 and 27830——27846.

As a matter of fact, when $m \geqslant 17$, the truth seems to be the following :

Theorem II : *When* m $\geqslant$ 17, *there are any number of sets of* m *consecutive integers such that there is no integer in the set, which is prime to all the rest in the set.*

I have not succeeded in proving theorem II ; but I have verified that it is true till $m = 430$. The method of verification is also indicated.

I arrived at theorem I in my attempt to prove that the product of m consecutive integers cannot be a perfect power. For some time I was under the impression that it would be universally true. I was able to prove [lemma (2)] that if the theorem is true when m is odd, then it is true for the next even integer. This result increased my hope. So I made many attempts to extend the result from an even integer to the succeeding odd integer, but only in vain. At last I arrived at the first set given above for $m = 17$.

The theorem itself is curious in that it stops at 16. But the method of proof is still more curious ; because the method of induction applies from an odd integer to the next higher even integer, but it fails from an even integer to the next higher odd integer. I wonder whether such a curious phenomenon in induction happens anywhere else.

* This formed a part of my Thesis for the M.Sc. degree of the Madras University.

II. Lemmas

Lemma (1): If among the integers $n, n+1, \cdots, n+m-1$, there is one number k which is prime to all the rest, then every prime divisor of k is greater than or equal to $(m+1)/2$.

Let p be a prime divisor of k.

Then $k-p, k, k+p$ have got the common factor p.

Since k lies in $(n, m+n-1)$ and prime to all the rest, $k-p$ and $k+p$ should fall outside this interval.

So (1) $k-p \leqslant n-1$ and (2) $k+p \geqslant n+m$.

Subtracting (1) from (2), we get

$$2p \geqslant m+1. \quad \text{So } p \geqslant (m+1)/2.$$

Lemma (2): If the theorem is true when $m = 2r+1$ and $r \geqslant 2$, then it is true for $m = 2r+2$ also.

A C B D

. . . . . .

Let (AB), (CD) denote the intervals $(n, n+2r)$, $(n+1, n+1+2r)$. By our assumption, there is one k in (AB), and one k' in (CD), which are prime to all the rest in their respective sets. If either $(k, \mathrm{D}) = 1$ or $(\mathrm{A}, k') = 1$, then either k or k' is prime to all to rest in the whole set (A, D). So the only unfavourable case is that simultaneously

$$(k, \mathrm{D}) = d > 1 \text{ and } (k', \mathrm{A}) = d' > 1. \qquad (1)$$

By lemma (1), every prime divisor of k and $k' \geqslant r+1$ and so odd; for $r \geqslant 2$. Hence k, k', d, d' all are odd. Again by lemma (1),

$$d \geqslant r+1 \quad \text{and} \quad d' \geqslant r+1.$$

So $k+2d$ and $k'-2d'$ fall outside the interval (AD).

Therefore

$$k+d = \mathrm{D} \text{ and } k'-d' = \mathrm{A}.$$

Consequently, since k and k are odd, D and A are even. But $\mathrm{D}-\mathrm{A} = 2r+1$. So one of D and A is odd which is against our conclusion. So our assumption (1) is wrong. From this and our first conclusion, the lemma follows.

Lemma (3): When $m \geqslant 4$, if k and k' are in and prime to all the rest in (AB), (CD) respectively,

A	C		B	D
.	.	. . . . .	.	.
n	$n+1$		$(n+m-1)$	$n+m$

and k and k' are divisible by p,

then $k = k'$.

By lemma (1), $p \geqslant (m+1)/2$.

Hence, since $m \geqslant 4$, k, k' and p are odd.

Therefore, $k-p$ and $k+p$ are even, and $k-2p$, $k+2p$ fall outside (AD). Hence if $p/(k, k')$, then $k = k'$.

Lemma (4): If p is any odd prime, then among m consecutive integers, p can divide at most $[1+(m-1)/2p]$ odd numbers.

If we assume that the first number is odd and a multiple of p, the number of odd multiples of p in the rest is $[(m-1)/2p]$. This is the most favourable case.

III. Proof of Theorem I

Now we are in a position to prove our main theorem.

We consider a set of m consecutive integers. If $p \geqslant m$ and T be a number in the set divisible by p, then, $T-p$ and $T+p$ fall outside the interval. Hence T cannot have the common factor $p \geqslant m$ with any other integer in the set.

Therefore in proving the theorem, it is enough if we consider the divisibility with respect to primes $\leqslant m-1$ only. (2)

Further by lemma (2), it is enough if we prove the theorem for

$$m = 2, 3, 4, 5, 7, 9, 11, 13 \text{ and } 15. \tag{3}$$

Case i: $m = 2, 3$.

Since n is prime to $(n-1)$ and $(n+1)$, the theorem follows at once.

Case ii: $m = 4$.

In this case we have to consider the divisibility with respect to 2, 3 only.

$$\begin{array}{cccc} 2 & & 2 & \\ \cdot & \cdot & \cdot & \cdot \end{array}$$

Let the four dots represent four consecutive integers. Let the first and the third be divisible by 2. Now 3 can divide only one of the numbers represented by the two blank points. Hence one number is divisible by neither 2 nor 3. So, that number is prime to all the rest. Consideration of symmetry leads us to the conclusion that the result of the other alternative with respect to the divisibility by 2 is the same.

In considering other cases, it is always assumed that the theorem is true for the previous case. Hence in the following,

A	C		B	D
.	.	. . . . .	.	.
n	$n+1$		$(n+m-2)$	$(n+m-1)$

there is an integer k in (AB) and k' in (CD), which are prime to all the rest in the respective sets. Let p be a prime divisor of k or k'. Then by lemma (1), $p \geqslant m/2$. Therefore, if p be a possible prime factor of either k or k', which is less than m, then values of p for m are given by the following table :

$m=$	5	7	9	11	13	15
$p=$	3	5	5, 7	7	7, 11	11, 13

Case iii : $m = 5, 7, 11$.

If k and k' coincide, then k is prime to all the rest in (AD). Hence the only unfavourable case is that k and k' are different. From the above table, there is only one possible prime factor $< m$, for k, k'. So by lemma (3), one of k, k' is divisible by no prime $< m$. From (2), it follows that that particular number is prime to all the rest in (AD).

Case iv : $m = 9$.

In this case, the only unfavourable case is when either (k, D) $= 5$ and (k', A) $= 7$, or the reverse. Since we are concerned with divisibility only, the order is immaterial, and so, it is enough if we consider only one case.

Since $k' - 14 <$ A and $k + 10 >$ D, A $= k' - 7$ and D $= k + 5$.

By lemma (2), k' is odd ; so A is even.

Therefore divisibility with respect to 2, 5, 7 is as follows :

A	C	K		B (=K')	D
.	. .	. . . .	.	.	.
2, 7	2	5 2	2	7	2, 5

Now there are two blank points and there is only one prime 3 is at our disposal. Since the difference between them is 4, if we assume that one number is divisible by 3, then the other is not divisible by 3. Hence one of these two blank points* is not divisible 2, 3, 5 or 7. Hence that number is prime to all the rest in the set. So the theorem is proved in this case, if it is true for 8.

Case v : $m = 13$.

Arguing out as in iv, in the most unfavourable case, we get the arrangement with respect to divisibliity by 2, 7, 11 as follows :

---

* Since there is no room for misunderstanding, number and point are used indifferently.

A C B D

. . . . . .

2 2 2 7 2 2 2 11 2

Now the distance between the extreme blank points is 8. Therefore by lemma (4), 5 divides at most one, and 3 at most two blank points. But there are four blank points. So at least one blank is not divisible by any prime < 13. Hence the theorem is true for 13, if it is true for 12.

Case vi : $m = 15$.

Arguing out as in iv, in the most unfavourable case, we arrive at the following scheme with respect to the divisibility by 2, 11, 13 :

A C B D

. . . . . (4)

2 2 11 2 2 2 2 2 13 2

Number of points in the interval terminated by the extreme blank points is 11. Therefore by lemma (4), 7 will cover only one blank point, and 5 can cover at most 2 blank points, and that is when it covers the extreme ones. So when 5 covers 2 blank points, for the divisibility with respect to 2, 5, 11, 13 we get the scheme :

. . . . . .

2 5 2 11 2 2 2 2 5 2 13 2

Now the interval terminated by the extreme blank points contains only five points. So by lemma (4), 3 and 7 can cover at most one blank point each. Hence one blank point is left uncovered. Therefore the only unfavourable case is the scheme in which 5 does not cover the extreme blank points in (4). In this case, by lemma (4), 7 can cover only one blank point, and 3 only two blank points. So in this case 3, 5, 7 can cover only four blank points, while there are five such points. Therefore, the theorem is true for 15 if it is true for 14.

Thus by combining the results in the above six cases with the lemma (2), we arrive at the theorem I.

Section IV

In this section I prove that theorem II is true when $17 \leqslant m \leqslant 430$.

Write down all the numbers from 1 to 430 (see the table at the end of the paper). Insert the primes 2, 3, 13 against 1, 2, 4 respectively. From the number 1, count 2 by 2, and cut out the resulting numbers. From the number 2, count 3 by 3 and cut the resulting numbers. Starting from the number 4, count 13 by 13 and cut the resulting numbers. Now, against

6, the first unmarked number, insert 5, and counting from it 5 by 5, mark out the resulting numbers. In this way, apply the Sieve of Eratosthenes in this particular manner by inserting the primes in order except 13 which we have inserted already. Call the numbers which necessitate the insertion of a new prime against them, 'gap numbers' or 'artificial primes'. From the table 1, 2, 4, 6, 10, 12, 18, 22, etc., are gap numbers. Again from the table, we see that, after 4, each gap number is greater than or equal to the prime inserted increased by one. If a is a gap number after 4, and p is the prime inserted against it, then, since $a - p \geqslant 1$, there is another number less than a which will be marked by p when counted backwards. That is, if a is divisible by p then there is another number less than a, which is also divisible by p. But when the number is less than 17, there is only one number less than or equal to it, which is divisible by 13. On the other hand, if n is greater than or equal to 17, for every prime p marked against the gap numbers, there are at least two numbers $\leqslant n$, which are marked by p. Now if we suppose 1 represents x, 2 represents $x + 1$, etc., then we can find x such that x satisfies the congruences, taking the table to be a congruence, the modulii being the primes marked against gap numbers. Hence if $430 \geqslant m \geqslant 17$, then among x, $x + 1$, $\cdots$, $x + m - 1$, there is no number which is prime to all the rest in the set. Thus the theorem is proved till $m = 430$.

In this way, with the help of a prime number table, one can verify as far as the table goes. In the accompanying table, upto 430, we require primes upto 281 only. So we have got 22 primes (from 282 to 430) in reserve. It is easy to show that the number of gap numbers is infinite. As in the case of primes, we can ask all questions about groups of gap numbers. Of course they are very difficult and artificial. If $N(m)$ is the number of exceptional sets of length m in the interval $(o, m!)$, the order of $N(m)$ also raises many interesting but difficult questions.

Table for the verification of Theorem II as far as $m = 430$

(*Note.*—Only gap numbers are given)

1	2	102	73	244	179
2	3	112	79	268	181
4	13	114	83	274	191
6	5	118	89	282	193
10	7	124	97	310	197
12	11	130	101	312	199
18	17	132	103	322	211
22	19	138	107	334	223
28	23	142	109	340	227
40	29	148	113	348	229
42	31	162	127	354	233
48	37	168	131	370	239
54	41	172	137	372	241
58	43	180	139	378	251
64	47	184	149	384	257
70	53	198	151	390	263
72	59	202	157	400	269
84	61	204	163	412	371
88	67	208	167	424	281
90	71	240	173		

GENERALISATION OF A THEOREM OF MANGOLDT*

By S. S. Pillai

(From the Department of Mathematics, Annamalai University)

Received December 12, 1939

(Communicated by Prof. B. S. Madhava Rao)

On page 571 of *Primzahlen*, Prof. Landau says " ....Bereits die erste, zuerst von Herrn von Mangoldt bewiesene, nicht triviale Abschatzung

$$L(x) = 0(x)$$

besagt ein wichtiges zahlentheortisches Gesetz :—

Esgibt bis x asymptotisch ebensoviele zahlen, welche aus einer geraden Anzahl von Primfaktoren zusammengesetzt sind, als solche, die aus einer ungeraden Anzahl von Primzahlen bestehen ".

Let $N_{r,t}(x)$ denote the number of numbers not exceeding x, whose number of prime factors belong to the residue class t modulus r. Further let $N'_{r,t}(x)$ be the number of such square free numbers. Then the above theorem is equivalent to

$$N_{2,1}(x) \sim N_{2,0}(x) \sim x/2.$$

Further Mangoldt proves that $N'_{2,1}(x) \sim N'_{2,0}(x)$. In this paper these results are generalised for prime values of r, namely, it is proved that

$$N_{p,t}(x) \sim x/t \qquad (t = 0, 1, \cdots, p-1) \tag{1}$$

$$N'_{p,t}(x) \sim \frac{6}{\pi^2} \cdot \frac{x}{p}. \tag{2}$$

In this connection Mobius function is generalised and a generalised form of zeta function is also introduced.

When I communicated the result to Mr. S. Chowla, he pointed[1] out that my proof could be modified to prove the result in all cases. For the sake of completeness Mr. Chowla's result is also given in the end of the paper as an appendix.

In a paper entitled " Zur Theorie der quadratfrei zahlen," published in Band 44, Heft 2 of *Mathematische Zeitschrift* (1938), Sigmund Selberg proves (2) without any restriction. Yet in view of the facts that my proof

* A part of my Thesis for the degree of D.Sc. of the Madras University, submitted in December 1933.

[1] From the date of Chowla's letter, I conclude, that I got these results in 1929.

differs entirely from his towards the end and Selberg does not consider $N_{r,t}(x)$, I believe that this paper is worth publication.[2]

II. Let us suppose that

(1) $\eta = e^{2\pi i/r}$;

(2) $\rho(n)$ = the number of different prime factors of n;

(3) $t(n)$ = the total number of prime factors of n, where each factor is counted according to its multiplicity;

(4) $\mu_r(1) = 1$,
$\mu_r(n) = 0$, when n is not squarefree,
$u_r(n) = \eta^{\rho(n)}$, when n is squarefree;

(5) $M_r(x) = \sum_{n=1}^{x} \mu_r(n)$;

(6) $g_r(x) = \sum_{n=1}^{x} \frac{\mu_r(n)}{n}$.

(7) $H_r(x) = \sum_{n=1}^{x} \mu_r(n) \log n$;

(8) $\lambda_r(n) = \eta^{t(n)}$;

(9) $L_r(x) = \sum_{n=1}^{x} \lambda_r(n)$;

(10) $A_r(n) = (-1)^m \cdot \eta^m \log p, \cdots$ when $n = p^m$
$A_r(n) = 0$, when n is not the power of a prime;

(11) $\psi_r(x) = \sum_{n=1}^{x} A_r(n)$; and

(12) $\xi_r(s) = \prod_{p} (1 + \eta/p^s)^{-1}$, when the real part of $s > 1$.

Then

(13) $$\frac{\xi'_r(s)}{\xi_r(s)} = -\sum_{n=1}^{\infty} \frac{A_r(n)}{n^s}$$

and (14) $$\frac{1}{\xi_r(s)} = \sum_{n=1}^{\infty} \frac{\mu_r(n)}{n^s}.$$

III. In this paragraph we shall prove several lemmas.

Lemma (i)

$$\psi_r(x) \sim -\eta x.$$

[2] The rest of the paper stands as it was submitted for D.Sc. degree.

From II, (10),

$$\psi_r(x) = \sum_1^x A_r(n) = \sum_{p^m \leqslant x} (-1)^m \cdot \eta^m \log p, \text{ from (8)}$$

$$= -\eta \sum_{p \leqslant x} \log p + O\left\{\sum_{\substack{p^m \leqslant x \\ m \geqslant 2}} \log p\right\}$$

$$= -\eta \sum_{p \leqslant x} \log p + O\ \sqrt{(x)}$$

$$\sim -\eta x.$$

Lemma (ii).

$$-H_r(x) = \sum_{n=1}^x \mu_r(n) \cdot \psi_r(x/n).$$

Now, when the real part of $s > 1$,

$$-\Sigma \frac{\mu_r(n) \log n}{n^s} = -\frac{\xi'_r(s)}{\{\xi_r(s)\}^2} = \frac{1}{\xi_r(s)} \times \left\{-\frac{\xi'_r(s)}{\xi_r(s)}\right\}$$

$$= \Sigma \frac{\mu_r(n)}{n^s} \times \Sigma \frac{A_r(n)}{n^s}, \text{ from (13) and (14).}$$

So

$$-\mu_r(n) \log n = \sum_{d|n} \mu_r(d) \cdot A_r(n/d).$$

Hence

$$-H_r(x) = \sum_{n=1}^x \sum_{d|n} \mu_r(d) \cdot A_r(n/d)$$

$$= \sum_{n=1}^x \mu_r(n) \sum_{m=1}^{x/n} A_r(m)$$

$$= \sum_{n=1}^x \mu_r(n)\ \psi_r(x/n) \text{ from (11).}$$

Lemma (iii) :

$$\sum_{d|n} \mu_r(d) = (1+\eta)^{\rho(n)}.$$

Now

$$\sum_{d|1} \mu_r(d) = \mu_r(1) = 1 = (1+\eta)^0 = (1+\eta)^{\rho(1)}.$$

Let

$$n = p_1^{\alpha_1} \cdot p_2^{\alpha_2} \cdots p_\rho^{\alpha_\rho}, \text{ where } n \geqslant 2.$$

In the above, there are 2^ρ non-vanishing terms which correspond to the divisors

$$d = p_1^{\beta_1} \cdot p_2^{\beta_2} \cdots p_\rho^{\beta_\rho}, \text{ where } \beta_s = 0 \text{ or } 1 \text{ and } s = 1, 2, \cdots, \rho.$$

So we get one term equal to 1, when $d = 1$,

$\binom{\rho}{1}$ terms each equal to η, when $d = p_s$,

$\binom{\rho}{2}$ terms each equal to η^2, when d is divisible by two primes, and so on.

Hence

$$\sum_{d|n} \mu_r(d) = 1 + \binom{\rho}{1} \cdot \eta + \binom{\rho}{2} \cdot \eta^2 + \cdots$$
$$= (1+\eta)^\rho.$$

Lemma (iv)

If $$K = \sum_{n=1}^{x} \sum_{d|n} \mu_r(d),$$

then $$|K| = 0(x \log x), \quad \text{when } r \geqslant 2.$$

From Lemma (iii)

$$|K| = \left| \sum_{n=1}^{x} (1+\eta)^{\rho(n)} \right| \leqslant \sum_{n=1}^{x} |(1+\eta)^{\rho(n)}|$$
$$\leqslant 1 + \sum_{\nu=1}^{\infty} |(1+\eta)^\nu| \, W_\nu(x),$$

where $W_\nu(x)$ denotes the number of numbers not exceeding x, which are composed of ν different prime of factors.

So $$|K| \leqslant 1 + \sum_{\nu=1}^{\infty} |(1+\eta)^\nu| \cdot \frac{L \cdot x}{\log x} \cdot \frac{(\log\log x + D)^{\nu-1}}{\underline{|\nu - 1}},$$

from (3·11) on page 269 of *Ramanujan's Collected Papers*, where L and D are positive constants.

Hence

$$|K| \leqslant 1 + L|1+\eta| \cdot \sum_{\nu=1}^{\infty} \frac{x}{\log x} \frac{\{(\log\log x + D) \cdot |1+\eta|\}^{\nu-1}}{\underline{|\nu - 1}}$$
$$= O\left\{\frac{x}{\log x} \cdot \text{Ex.}\,[|1+\eta| \cdot (\log\log x + D)]\right\}$$
$$= O\left\{\frac{x}{\log x} \cdot (\log x)^{|1+\eta|}\right\}$$
$$= O\left\{x \cdot (\log x)^{2\cos\frac{\pi}{r} - 1}\right\}$$
$$= o(x \log x);$$

for, $$|1+\eta| = \left|1 + \cos\frac{2\pi}{r} + i \sin\frac{2\pi}{r}\right| = 2\left|\cos\frac{\pi}{r}\right| < 2, \quad \text{when } r \geqslant 2.$$

So the lemma is proved.

Lemma (v).

If K denotes the same expression as in lemma (iv), then

$$K = x \cdot g_r(x) + O(x).$$

$$K = \sum_{n=1}^{x} \mu_r(n) \sum_{m=1}^{x/n} 1$$

$$= \sum_{n=1}^{x} \mu_r(n) \times \left[\frac{x}{n}\right] = \sum_{n=1}^{x} \frac{x \cdot \mu_r(n)}{n} + O\left(\sum_{n=1}^{x} 1\right)$$

$$= x \cdot g_r(x) + O(x).$$

Lemma (vi) :

$$g_r(x) = o(\log x).$$

From lemmas (iv) and (v),

$$x \cdot g_r(x) + O(x) = K = o(x \cdot \log x)$$

So $$x \cdot g_r(x) = o(x \cdot \log x).$$

Hence

$$g_r(x) = o(\log x).$$

Lemma (vii) :

$$H_r(x) = o(x \cdot \log x).$$

Let δ be a given small positive number. Then from lemma (i) we can choose a $\Delta = \Delta_0(\delta)$ such that when $x > \Delta$ and $n \leqslant \frac{x}{\Delta}$,

$$\left| \psi_r\left(\frac{x}{n}\right) + \eta \cdot \frac{x}{n} \right| < \frac{\delta x}{n}.$$

So for $x > \Delta$,

$$|H_r(x)| \leqslant \left| \sum_{n=1}^{x/\Delta} \mu_r(n)\, \psi_r\left(\frac{x}{n}\right) \right| + \left| \sum_{n > x/\Delta}^{x} \mu_r(n) \cdot \psi_r(x/n) \right|$$

$$\leqslant \left| \sum_{n=1}^{x/\Delta} \mu_r(n) \left\{ \psi_r\left(\frac{x}{n}\right) + \eta \cdot \frac{x}{n} \right\} \right| + \left| \sum_{n=1}^{x/\Delta} \mu_r(n) \cdot \eta \cdot \frac{x}{n} \right|$$

$$+ \left| \sum_{n > x/\Delta}^{x} \mu_r(n) \cdot \psi_r(x/n) \right|$$

$$< \delta \cdot \sum_{n=1}^{x/\Delta} \frac{x}{n} + x \cdot |g_r(x/\Delta)| + \sum_{n > x/\Delta}^{x} |\psi_r(\Delta)|$$

$$< \delta x \log x + x\,|g_r(x/\Delta)| + x \cdot |\psi_r(\Delta)|$$

$$= \delta x \log x + o(x \log x) + O(x \cdot \Delta), \text{ from lemmas (i) and (vi).}$$

Now, δ is an arbitrary constant and Δ is independent of x. Hence

$$|H_r(x)| = o(x. \log x).$$

Lemma (viii)

$$M_r(x) = o(x).$$

Now,

$$|M_r(x)| = \left| 1 + \sum_{n=2}^{x} \{H_r(n) - H_r(n-1)\}/\log n \right|$$

$$= \left| 1 + \sum_{n=2}^{x} H_r(n)\{1/\log n - 1/\log(n+1)\} + H_r(x)/\log([x]+1) \right|$$

$$= O\left\{ \sum_{n=2}^{x} |H_r(n)|/n(\log n)^2 \right\} + O\{H_r(x)/\log x\}$$

$$= O\left\{ \sum_{n=2}^{x} (n \log n)/n \log^2 n \right\} + o(x), \quad \text{from lemma (vii)}$$

$$= O\left\{ \sum_{n=2}^{x} 1/\log n \right\} + 0(x)$$

$$= o(x).$$

Lemma (ix) :

$$\lambda_r(n) = \sum_{d^2/n} \mu_r(n/d^2) \cdot \eta^{2\cdot t(d)}.$$

When the real part of $s > 1$,

$$\sum \frac{\lambda_r(n)}{n^s} = \prod_p \left(1 + \frac{\eta}{p^s} + \frac{\eta^2}{p^{2s}} + \cdots\right)$$

$$= \prod_p \left(1 - \frac{\eta}{p^s}\right)^{-1} = \prod_p \left\{(1+\eta/p^s)(1-\eta^2/p^{2s})^{-1}\right\}$$

$$= \{\prod_p (1+\eta/p^s)\} \cdot \prod_p (1-\eta^2/p^{2s})^{-1}$$

$$= \left\{\sum \frac{\mu_r(n)}{n^s}\right\} \times \left\{\sum \frac{\eta^{2t(u)}}{n^{2s}}\right\}.$$

Equating the coefficients of n^{-s} on both sides, we arrive at the lemma.

Lemma (x) :

$$I_r(x) = o(x).$$

Now,

$$I_r(x) = \left| \sum_{n=1}^{x} \sum_{d^2/n} \mu_r(n/d^2) \cdot \eta^{2t(d)} \right|, \quad \text{from lemma (ix)}$$

$$= \left| \sum_{m=1}^{\sqrt{x}} \eta^{2t(m)} \cdot \sum_{n=1}^{x/m^2} \mu_r(n) \right|$$

$$= \left| \sum_{n=1}^{\sqrt{x}} \eta^{2t(n)} \cdot M_r(x/n^2) \right|$$

$$\leqslant \sum_{n=1}^{\sqrt{x}} |\, M_r\,(x/n^2)\,|$$

$$= \sum_{n=1}^{\sqrt{x}} 0\,(x/n^2), \quad \text{from lemma (viii)}$$

$$= o\left(x \sum_{1}^{\infty} \frac{1}{n^2}\right) = o\,(x).$$

IV. Now we are in a position to prove our theorems.

THEOREM I: *When* p *is a prime number and* t $= 1, 2, \cdots$ *or* p,

$$N_{p,t}\,(x) \sim x/p$$

Now

$$(15) \quad \sum_{t=1}^{p} \eta^t\, N_{p,t}\,(x) = L_r\,(x) = o\,(x), \quad \text{from lemma (x), and}$$

$$(16) \quad N_{p,t}\,(x) = x.$$

Since p is a prime number, the equation

$$1 + x + \cdots + x^{p-1} = 0$$

is irreducible.

(17) So η cannot be the root of any lower degree equation when r is a prime.

(18) Let $\quad B_1 + B_2\eta + \cdots + B_p \cdot \eta^{p-1} = 0$

(19) But $\quad 1 + \eta + \cdots + \eta^{p-1} = 0.$

Multiply (19) by B_p and from the result subtract (18).

Then

$$(20) \quad (B_1 - B_p) + (B_2 - B_p)\,\eta + \cdots + (B_{p-1} - B_p)\,\eta^{p-2} = 0.$$

Unless $B_1 = B_2 = \cdots = B_p$, (17) and (20) contradict each other.

Hence,

(21) if $\quad B_1 + B_2\,\eta + \cdots + B^p\,\eta^{p-1} = 0,$

then $\quad B_1 = B_2 = \cdots = B_p.$

Now from (15)

$$(22) \quad N_{p,1}\,(x) + N_{p,2}\,(x) \cdot \eta + \cdots + N_{p,p}\,(x) \cdot \eta^{p-1} = o\,(x)$$

and from (16)

$$(23) \quad N_{p,1}\,(x) + N_{p,2}\,(x) + \cdots + N_{p,p}\,(x) = x.$$

Hence from (21) to (23), the theorem follows.

Similarly proceeding, we can prove

THEOREM II: *When* p *is a prime and* t $= 1, 2, \cdots$ *or* p, *then*

$$N'_{p,t}\,(x) \sim 6 \cdot x/p \cdot \pi^2.$$

APPENDIX

When I communicated this result to Mr. S. Chowla, he pointed out that a slight modification of my proof would remove the restriction that r is a prime number. For the sake of completeness, I give his generalisation also.

Let $$\eta' = e^{2m\pi i/r}, \qquad (m = 1, 2, \cdots r-1)$$

and $$L'_r(x) = \sum_{n=1}^{x} \lambda'_r(n), \quad \text{where } \lambda'_r(n) = \eta'^{t(n)}.$$

Then the same proof given in the body of the paper leads to the result

$$L'_r(x) = o(x).$$

This means that

C. $$\sum_{t=1}^{r} \eta'^{t} N_{r,t}(x) = o(x).$$

So

D. $$\sum_{t=1}^{r} \eta'^{t-a} \cdot N_{r,t}(x) = o(x).$$

From this, by putting m equal to $1, 2, \cdots r-1$, in succession in D, we have,

$$\eta^{1-a} N_{r,1}(x) + \eta^{2-a} N_{r,2}(x) + \cdots + N_{r,a}(x) + \cdots + \eta^{r-a} N_{r,r}(x) = o(x)$$

$$\eta^{2(1-a)} N_{r,1}(x) + \eta^{2(2-a)} N_{r,2}(x) + \cdots + N_{r,a}(x) + \cdots + \eta^{2(r-a)} N_{r,r}(x) = o(x)$$

$$\eta^{3(1-a)} N_{r,1}(x) + \eta^{3(2-a)} N_{r,2}(x) + \cdots + N_{r,a}(x) + \cdots + \eta^{3(r-a)} N_{r,r}(x) = o(x)$$

. . . . . .

. . . . . .

$$\eta^{(r-1)(1-a)} N_{r,1}(x) + \eta^{(r-1)(2-a)} N_{r,2}(x) + \cdots + N_{r,a}(x) + \cdots + \eta^{(r-1)(r-a)} N_{r,r}(x) = o(x)$$

Further, $$N_{r,1}(x) + N_{r,2}(x) + \cdots + N_{r,a}(x) + \cdots + N_{r,r}(x) = x.$$

Adding the above by columns and making use of (C) we get that

$$r \cdot N_{r,a}(x) = x + o(x)$$

So, $$N_{r,a}(x) = x/r + o(x).$$

Hence the result is generalised.

ON THE POLYNOMIAL $\pi_n(x)$

By R. S. Varma
(*Department of Mathematics, University of Lucknow*)

Received December 12, 1939
(Communicated by Prof. B. S. Madhava Rao)

The polynomial $\pi_n(x)$, suggested by A. Angelescu,[1] is defined by

$$\pi_n(x) = e^x \frac{d^n}{dx^n}[e^{-x} A_n(x)]$$

where

$$A_n(x) = (a_0, a_1, a_2, \cdots, a_n, x, 1)^n.$$

In a recent paper Mr. B. S. Sastry[2] has shown, among other results, that the polynomial $\pi_n(x)$ is the coefficient of $t^n/n!$ in the expansion of

$$\frac{1}{1-t} e^{-\frac{xt}{1-t}} \phi\left(-\frac{t}{1-t}\right)$$

where $\phi(z) = a_0 + \frac{a_1 z}{|1} + \frac{a_2 z^2}{|2} + \cdots$, *i.e.*, that

$$\frac{1}{1-t} e^{-\frac{xt}{1-t}} \phi\left(-\frac{t}{1-t}\right) = \sum_{n=0}^{\infty} \frac{t^n}{n!} \pi_n(x) \qquad (1)$$

a formula resembling

$$\frac{1}{1-t} e^{-\frac{xt}{1-t}} = \sum_{n=0}^{\infty} \frac{t^n}{n!} L_n(x) \qquad (2)$$

which is the well-known generating function for the Laguerre polynomial $L_n(x)$. The object of this note is to investigate the following relations between the polynomials $\pi_n(x)$ and $L_n(x)$:

(A) $$\sum_{r=0}^{n} \binom{n}{r} L_r(x) \frac{d^p}{dx^p}\{\pi_{n-r}(x)\} = \sum_{r=0}^{n} \binom{n}{r} \pi_r(x) \frac{d^p}{dx^p}\{L_{n-r}(x)\}$$

and $$0 < p < n$$

(B) $$\frac{\pi_n(u+v)}{n!} = \sum_{r=0}^{n} \frac{\pi_r(u)}{r!} \frac{L_{n-r}(v)}{(n-r)!} - \sum_{r=0}^{n-1} \frac{\pi_r(u)}{r!} \frac{L_{n-r-1}(v)}{(n-r-1)!}.$$

The result (A) is of a reciprocal nature while the second result may be taken as the addition theorem for the polynomial $\pi_n(x)$.

To prove the first result, we note that the relation (1), in consequence of (2), can be written in the form

$$\sum_{n=0}^{\infty} \frac{t^n}{n!} \pi_n(x) = \sum_{n=0}^{\infty} \frac{t^n}{n!} \mathrm{L}_n(x)\, \phi\left(-\frac{t}{1-t}\right). \tag{3}$$

Differentiating both sides of this p times with respect to x, we get

$$\sum_{n=0}^{\infty} \frac{t^n}{n!} \frac{d^p}{dx^p}\left\{\pi_n(x)\right\} = \phi\left(-\frac{t}{1-t}\right) \sum_{n=0}^{\infty} \frac{t^n}{n!} \frac{d^p}{dx^p}\left\{\mathrm{L}_n(x)\right\}$$

which by virtue of (3) gives that

$$\sum_{n=0}^{\infty} \frac{t^n}{n!} \mathrm{L}_n(x) \sum_{n=0}^{\infty} \frac{t^n}{n!} \frac{d^p}{dx^p}\left\{\pi_n(x)\right\} = \sum_{n=0}^{\infty} \frac{t^n}{n!} \pi_n(x) \sum_{n=0}^{\infty} \frac{t^n}{n!} \frac{d^p}{dx^p}\left\{\mathrm{L}_n(x)\right\} \tag{4}$$

If now we pick up the coefficients of t^n from either side of (4), we at once obtain the relation (A).

To establish the second result, write $u + v$ for x in (1). We have then

$$\sum_{n=0}^{\infty} \frac{t^n}{n!} \pi_n(u+v) = \frac{1}{1-t} e^{-\frac{ut}{1-t}} \phi\left(-\frac{t}{1-t}\right) e^{-\frac{vt}{1-}}$$

$$= (1-t) \sum_{n=0}^{\infty} \frac{t^n}{n!} \pi_n(u) \sum_{n=0}^{\infty} \frac{t^n}{n!} \mathrm{L}_n(v),$$

where we have used (1) and (2). The result (B) follows by equating the coefficients of t^n on either side.

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USE OF MERCURIC ACETATE IN ORGANIC PREPARATIONS

Part II. Some Experiments on its Use as an Oxidising Agent

By N. V. Subba Rao and T. R. Seshadri

(From the Department of Chemical Technology, Andhra University, Waltair)

Received December 18, 1939

Besides being used widely as a reagent for mercuration, mercuric acetate has been successfully employed as an oxidising agent.[1] Its action in this respect is said to be similar to that of chromic acid or permanganate and specially suited where a mild oxidising agent is required so that the oxidation may not proceed too far. It is obvious that an excess of the reagent and the sparingly soluble mercurous acetate which is one of the products of reaction, can both be removed easily. It has further been claimed that the sparingly soluble mercurous acetate can be collected and weighed and hence the progress of the reaction followed quantitatively.

Balbiano and his collaborators[2] found that certain olefines, *e.g.*, anethole, iso-safrole, methyl iso-eugenol, etc., which contain a propenyl group $-CH : CH \cdot CH_3$ react with mercuric acetate in aqueous solution giving rise to glycols of the general formula $-CHOH \cdot CHOH \cdot CH_3$ with the addition of two –OH groups at the double bond, the mercuric acetate being reduced to mercurous acetate. A similar observation has been made by Sanjiva Rao and Subrahmanyam[3] in regard to β-asarone. Safrole and methyl eugenol which contain an allyl group react with mercuric acetate forming a complex compound with the addition of a hydroxy group and an acetoxy mercury group at the double bond ($-CH_2 \cdot CHOH \cdot CH_2.HgOAc$).

Gadamer and his co-workers[4] have successfully employed mercuric acetate for isolating intermediate stages in the oxidation of alkaloids. Papaverine on oxidation yielded papaverinol and papaveraldine and *d*-canadine was converted into berberine. Windaus *et al.*[5] have employed this reagent in connection with sterols and have been able to obtain dehydro-ergosterol from ergosterol and ergostatrienol—*d* from di-hydro-ergosterol.

From the claims of the previous workers it seemed possible to follow the course of the oxidation reactions, using mercuric acetate, quantitatively by weighing the amount of mercurous acetate formed and it was thus hoped to obtain information regarding their mechanism. In order to test this, the best conditions suitable for the reaction and the behaviour of the reagent

in various solvents had to be studied in detail. Solutions in water, dilute acetic acid or in alcohol have been employed by previous workers. In all cases, it is necessary to add few drops of acetic acid in order to produce a clear solution and to prevent hydrolysis. The following sums up the behaviour of the common solvents. In the cold water, ethyl and methyl alcohols, dry or containing water, by themselves, produce no change. When boiled, however, there was considerable difference in their behaviour. Excepting dry methyl alcohol, all the others produced appreciable amounts of mercurous acetate. Hence this was chosen as the most suitable solvent; but it was soon realised that complications set in during the course of experiments on actual oxidations of well-known substances. Using benzoin and hydroquinone as typical examples, it was observed that mercurous acetate was produced far in excess of what could be expected from the quantities of benzil and quinone formed at the same time. It was therefore suspected that the solvent was taking a share in the reduction of mercuric acetate in the presence of the other more powerful reducing agents. That is, hydroquinone or benzoin acts also as an inducing agent in enabling the oxidation of methyl alcohol with mercuric acetate to take place. This inference was remarkably supported by experiments carried out using small quantities of hydroquinone or benzoin as an inducing agent under two sets of conditions: (i) at the boiling point of the solvent; (ii) at ordinary temperature in the presence of sunlight. Considerable amounts of mercurous acetate were formed thereby showing definitely that the solvents can undergo oxidation to an appreciable extent in the presence of these inducing agents. Hence the yield of mercurous acetate cannot indicate correctly the progress of oxidation of a substance when mercuric acetate is employed.

As a result of a number of experiments carried out in connection with the object mentioned above, convenient methods very suitable in the laboratory for the small-scale production of mercurous acetate in a crystalline and pure condition and of quinhydrone, quinone and benzil have been worked out. A number of substances containing the secondary alcoholic group such as iso-propyl alcohol, diphenyl carbinol, ethyl tartrate, menthol, quinine and cinchonine and cholesterol reduce mercuric acetate and deposit in considerable amounts the mercurous compound. This seems to be of general applicability for all compounds containing the CHOH group. In several cases, the products of oxidation could be identified; iso-propyl alcohol, diphenyl carbinol and cinchonine yielded acetone, benzo-phenone and cinchoninone respectively, though the yields were unsatisfactory. In the other cases, the reactions seemed to be complex and no definite oxidation products could be obtained.

Experimental

Effect of ordinary solvents on mercuric acetate.—In preparing solutions of mercuric acetate in water or alcohol, a few drops of glacial acetic acid were always added in order to prevent the hydrolysis of mercuric acetate. At the ordinary laboratory temperature, the solvents (water, ethyl alcohol, methyl alcohol, etc.) did not produce any appreciable amount of mercurous acetate when the solutions were kept in the dark for a few days. The results that were obtained regarding the action of the solvents on mercuric acetate both at the boiling point of the solvents and at the ordinary temperature exposed to sunlight in a quartz flask are tabulated below. Saturated

TABLE I. *Action of solvents on mercuric acetate at their boiling temperatures*

Solvent	Period of time employed	Yield of mercurous acetate
		g.
Water	24 hours	0·1*
Rectified spirit	,,	0·8
Absolute alcohol	,,	0·3
Anhydrous methyl alcohol ..	,,	Nil
Dilute methyl alcohol (90%) ..	,,	0·05

* The yield in the case of water is less probably due to the greater solubility of mercurous acetate in water than in alcohol.

TABLE II. *Action of very small quantities (about 1 m.g.) of inducing agents on anhydrous methyl alcoholic solution*

Boiling or exposure to sunlight	Inducing agent employed	Period of time employed	Yield of mercurous acetate
			g.
Boiling ..	Benzoin ..	10 hours	0·17
,,	Hydroquinone ..	,,	0·50
Exp. to sunlight ..	None ..	,,	0·03
,,	Benzoin ..	,,	0·45
,,	Hydroquinone ..	,,	1·0

solutions using 5 g. of mercuric acetate in various solvents were used in all the cases mentioned.

Preparation of pure mercurous acetate and benzil.—2 g. of benzoin were dissolved in the minimum amount of anhydrous methyl alcohol and to it was added a solution of mercuric acetate (6 g. in the same solvent 100 c.c.). When allowed to stand at the room temperature, the reaction proceeded very slow. The mixture was therefore heated under reflux, when a colourless crystalline solid began to separate rapidly. At the end of every 6 hours, this solid was filtered and the filtrate again refluxed. This process was repeated till no more of the crystalline solid separated (total time taken 36 hours). The colourless crystalline precipitate obtained was collected together, washed with hot methyl alcohol and dried (yield 4 g., about 80% conversion of the mercuric acetate). It was sparingly soluble in water and alcohol and on heating began to char at 300° C. without previous melting. It dissolved easily in dilute nitric acid and this solution gave a curdy white precipitate with a drop of hydrochloric acid. It turned black in the presence of sodium hydroxide producing mercury. The percentage of mercury in this compound was estimated [Found: Hg, 76·8 per cent.; Hg_2 (O CO CH_3)$_2$ requires Hg, 77·2 per cent.]. The sample therefore was pure mercurous acetate and the method is convenient for the preparation of pure mercurous acetate from mercuric acetate in the laboratory.

The filtrate from the mercurous acetate was coloured deep yellow. The solvent was distilled off and the yellow residue was washed with hot water to remove the excess of mercuric acetate and unreacted benzoin and finally the product was recrystallised from methylated spirits. Yellow needle-shaped crystals of benzil melting at 95° were thus obtained in a yield of only 40 per cent. (0·8 g.). It formed a diphenyl hydrazone melting at 225° C. A mixed melting point of the substance with benzil established its identity.

The above reaction was conducted more conveniently in hot aqueous medium, when benzil began to separate as a yellow liquid (its m.pt. being 95° C.) along with mercurous acetate. While hot, the aqueous layer was decanted off. The yellow residue remaining behind was purified by extraction with ether and recrystallisation from alcohol. The product was purer than in the previous case since unreacted benzoin was kept in solution in hot water; but there was no improvement in the yield of benzil.

Preparation of quinhydrone.—Hydroquinone (2 g.) dissolved in water (30 c.c.) was added to a similar solution of mercuric acetate (20 g. in 100 c.c.) and thoroughly shaken for a few minutes, when the colourless mixture began to turn brown. It was then repeatedly extracted with small amounts of

ether and the combined ether extract was evaporated. The residue separated as prisms with green metallic lustre (1·3 g.). The product was then purified by washing with small amounts of water, taking it up in ether and evaporating the ether solution. It melted at 171° C. and a mixed melting point determination with a pure sample of quinhydrone established its identity. The mercurous acetate that was obtained as a result of reduction was then filtered from the aqueous *layer* and washed with a small amount of alcohol to remove any adhering quinhydrone.

Preparation of quinone.—The above reaction was carried out by heating the mixture for half an hour at 80° C. on a water-bath and after cooling the mixture to the laboratory temperature, it was extracted with ether in small amounts repeatedly. The combined ether extracts on evaporation gave a yellow crystalline material which after recrystallisation was found to be quinone (yield: 0·7 g.) by its m.pt. (115° C.) and other properties. The aqueous *layer* contained in addition to mercurous acetate some globules of mercury.

When the reaction was carried out at the ordinary temperature but in the presence of sunlight for 3 hours the product of oxidation was quinone. It could be easily obtained by ether extracting the final mixture (yield: 0·5 g.).

Summary

Experiments have been conducted with a view to test if the progress of oxidation by mercuric acetate could be followed by weighing the amount of mercurous acetate precipitated from time to time. This procedure has been found to be not feasible since complications set in owing to the solvent also undergoing oxidation induced by the presence of other substances. It has been found that most compounds containing –CHOH group produce mercurous acetate in methyl alcoholic solution and the oxidation products could be identified. Convenient methods for the preparation of benzil, quinhydrone, quinone and mercurous acetate in a pure condition in the laboratory are described.

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ULTRASONIC VELOCITIES AND ADIABATIC COMPRESSIBILITIES OF SOME ORGANIC LIQUIDS

By J. Bhimasenachar and K. Venkateswarlu
(From the Department of Physics, Andhra University, Waltair)

Received December 29, 1939
(Communicated by Prof. S. Bhagavantam)

1. Introduction and Experimental Details

The standard Hartley circuit is employed for producing piezo-electric oscillations in an X-cut quartz crystal, the fundamental frequency of which is about 1·6 M.C. The optical and other arrangements are of the usual type. A mercury pointolite lamp is used as the source and λ 5460 is isolated by a Zeiss filter. A Philip's Heterodyne wavemeter capable of measuring frequencies correct to 0·2 per cent. is used for measuring the frequency of the oscillator.

In almost all the organic liquids and the essential oils studied, the velocities are measured at about 4·3, 7·2, 10·0 and 13·0 M.C. and their mean is taken. The temperature at which the measurements are made, is noted with a thermometer *in situ*. Densities of the samples used for measuring the velocities are determined with a density bottle immediately after the velocity determination is over.

The liquids and essential oils used are manufactured either by Merck or Kahlbaum or Theodar Schuchardt. Almost all the liquids are redistilled and that portion which is collected at the appropriate boiling point is employed. Formalin and a few other liquids obtained from freshly opened bottles have not been distilled. In the case of the essential oils, the distillate collected at the temperature appropriate to the boiling point of the chief constituent is employed in the investigation.

2. Results

Results of measurements with pure liquids are tabulated in Table I and those obtained with the essential oils in Table II. Compressibilities obtained by other workers by employing piezometric methods are compared with the results of the present investigation in Table IV. The sound velocity is measured for the first time by the authors using the ultrasonic method in all the liquids listed in this paper.

TABLE I

Ultrasonic Velocities and Adiabatic Compressibilities

Liquid	Chemical Formula	Temperature °C.	Density	Velocity m./s.	Compressibility $\times 10^6$
Benzyl acetate ..	$C_6H_5 \cdot CH_2 \cdot O \cdot CO \cdot CH_3$	26·5	1·049	1470	44·7
Phenyl acetate ..	$CH_3 \cdot CO \cdot OC_6H_5$	27·5	1·074	1438	45·6
Formalin (Aq. Soln.)..	$H \cdot CHO$	27·5	1·067	1625	35·9
Paraldehyde ..	$(C_2H_4O)_3$	28·0	0·991	1197	71·3
Anisaldehyde ..	$C_6H_4(OCH_3) \cdot CHO$	28·0	1·116	1577	36·5
Methyl iodide ..	CH_3I	27·0	2·261	860	60·6
Ethyl iodide ..	C_2H_5I	25·0	1·912	895	66·1
Allyl iodide ..	$CH_2 : CH \cdot CH_2I$	28·0	1·792	846	78·9
Dimethyl aniline ..	$C_6H_5 \cdot N(CH_3)_2$	26·0	0·950	1550	45·0
Diethyl aniline ..	$C_6H_5 \cdot N(C_2H_5)_2$	28·0	0·927	1516	47·5
Methyl-ethyl-ketone	$CH_3 \cdot CO \cdot C_2H_5$	30·0	0·799	1244	81·9
Nitromethane ..	$CH_3 \cdot NO_2$	28·0	1·125	1359	48·8
Benzonitrile ..	$C_6H_5 \cdot CN$	28·0	0·995	1581	40·7
m-Chlorotoluene ..	$C_6H_4Cl \cdot CH_3$	27·0	1·062	1310	55·5

TABLE II

Ultrasonic Velocities and Adiabatic Compressibilities

Oil used	Chief constitutent	Chemical formula	Temperature °C.	Density	Velocity m./s.	Compressibility $\times 10^6$
Eucalyptus oil ..	Cineol	$C_{10}H_{18}O$	27·5	0·914	1309	64·7
Cajeputi oil ..	,,	,,	27·0	0·910	1326	63·3
Citronellæ oil ..	Citronellal	,,	27·0	0·859	1394	60·7
Camphor oil ..	Camphorol	$C_9H_{16}O$	26·0	0·917	1475	50·7
Coriandri oil ..	*d*-Linalol	$C_{10}H_{18}O$	26·5	0·861	1390	60·9
Juniperi baccarum oil ..	α-Pinene	$C_{10}H_{16}$	28·5	0·846	1298	71·0

3. *Discussion*

Pure Liquids.—The ultrasonic velocity is higher in the aromatic acetates (as may be seen from benzyl and phenyl acetates of Table I) than in the case of aliphatic acetates.[1] This result is in agreement with the general rule that the ultrasonic velocity is usually greater in aromatic than in aliphatic compounds.

The following iodides listed in Table III show that with increasing carbon content, the ultrasonic velocity as well as the adiabatic compressibility increase. At the same time the density decreases.

TABLE III

Liquid	Temperature °C.	Density	Velocity in m./s.	Compressibility × 10^6
Methyl iodide ..	27	2·261	860	60·6
Ethyl iodide ..	25	1·912	895	66·1
Butyl iodide[1] ..	28	1·616	959	67·3

One would expect the adiabatic compressibility to decrease with increasing ultrasonic velocity but in this series, the reverse takes place. This is due to the extraordinary control exercised by the density which decreases very rapidly. The relatively low sound velocity obtained in this series which appears to be a characteristic feature of all iodides may also be noted.

It is interesting to note that the ultrasonic velocity is very high in formalin which is a 40 per cent. aqueous solution of formaldehyde. This is much higher than even the velocity obtained in the aromatic aldehydes.[2] This may be due to the well-known fact that formaldehyde does not exist as such in aqueous solutions.

Essential Oils.—In the case of eucalyptus and cajeputi oils, the chief constituent being the same, the density, ultrasonic velocity and adiabatic compressibility are nearly the same as they ought to be. The small differences are most probably due to small quantities of impurities that might have gone over into the distilled samples.

Comparison with Compressibilities Obtained by Piezometric Methods.—The available data are collected together and compared in Table IV.

[1] Bergmann, *Ultrasonics*, (Bell & Sons), 1938, p. 126.
[2] Parthasarathy, *Proc. Ind. Acad. Sci.*, 1936, **4**, 213.

TABLE IV

Liquid	Other workers		Authors	
	Temperature °C.	Compressibility × 10^6	Temperature ° C.	Compressibility × 10^6
Benzyl acetate ..	32·8	50·3*	26·5	44·7
Formalin ..	31·6	45·5*	27·5	35·9
Paraldehyde ..	33·4	86·8*	28·0	71·3
Cajeputi oil ..	26·7	68·8†	27·0	63·3
Eucalyptus oil ..	28·0	74·0†	27·5	64·7
Citronellæ oil ..	25·1	69·4†	27·0	60·7
Coriandri oil	26·7	71·7†	26·5	60·9

* Philip, *Proc. Ind. Acad. Sci.*, 1939, **9**, 114.

† Dakshinamoorthy, *Ibid.*, 1937, **5**, 397.

From Table IV it may be seen that the values of Philip and Dakshinamoorthy are somewhat higher than those of the authors. The discrepancies may be due to the fact that the methods employed by Philip and Dakshinamoorthy do not presumably give compressibility values which are strictly adiabatic. The temperatures at which the two sets of measurements have been made are also different. Moreover, in the case of the essential oils, Dakshinamoorthy used a vertical type of piezometer which gives high values due to the presence of dead space. These factors apparently provide the explanation for the relatively large values obtained by the earlier authors who used piezometric methods.

4. *Summary*

Ultrasonic velocities are reported for fourteen organic liquids and the chief constituents of six essential oils. All these substances are investigated here for the first time. From these data, the compressibilities are calculated and compared with the compressibilities obtained earlier in some cases by other methods. A brief discussion of the results is given.

The authors wish to thank Prof. S. Bhagavantam for his kind encouragement during the course of this work. One of them (J.B.) is indebted to the Andhra University for the grant of a research fellowship.

RAMAN EFFECT AND CHEMICAL CONSTITUTION

Influence of Constitutive and Other Factors on the Double Bonds in Organic Compounds

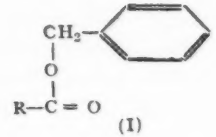
Part III. Effect of the Benzyl Group on the C = O Bond in Esters

By G. V. L. N. Murty and T. R. Seshadri

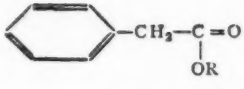
(From the Department of Chemistry, Andhra University, Waltair)

Received December 4, 1939

In a previous communication (Part II)[1] it was shown that a phenyl group attached directly to the carbon of the C = O as in the esters of aromatic acids and in aromatic ketones markedly lowers the frequency of the C = O bond whereas the same group attached to the oxygen of the COO as in phenyl esters definitely increases it. These phenomena were explained as due to the existence of resonance in the first group of compounds and in the second group as due to the reinforcement by the phenyl nucleus of the normal electromeric polarisation of esters towards the C = O resulting in greater electron acceptance. That the explanation is correct and that the marked changes in the C = O frequencies are neither due to the bulk of the phenyl group nor due to the general inductive effect is confirmed by the study of the benzyl esters of various acids (I) and the esters of phenyl acetic acid (II) recorded in this paper. The new feature introduced in these compounds is the presence of a CH_2 group adjacent to the phenyl ring which prohibits the transmission of electromeric effects from it to the carbonyl group.



(I)



(II)

Benzyl esters as a class do not seem to have received much attention in connection with the Raman Effect. Benzyl acetate[2] appears to be the only compound so far investigated and here too the results are not satisfactory since very few lines have been recorded and the Raman line corresponding

to the C = O bond has been missed. This substance has therefore been reinvestigated and the spectra of the benzyl esters of propionic, benzoic and cinnamic acids have been studied in detail. The results have been compared with those relating to the corresponding phenyl and ethyl esters. Further, the spectra of the phenyl esters of propionic and phenyl acetic acid have been studied in detail and those of ethyl propionate and ethyl phenyl acetate reinvestigated. Particulars regarding experimental procedure are the same as recorded in Part II. Spectra of a few typical cases are reproduced at the end of the paper and the C = O frequencies are indicated by arrows.

Preparation of the Esters.—Ethyl propionate and the ethyl ester of phenyl acetic acid were prepared by heating mixtures of the appropriate acid and alcohol along with a few c.c. of concentrated sulphuric acid. Phenyl propionate was obtained by heating dry phenol with sodium propionate and propionic anhydride at 160° in an oil-bath for 4 hours. For producing the phenyl ester of phenyl acetic acid the acid chloride was first obtained by the action of thionyl chloride and was made to react with dry phenol in the presence of pyridine. All the esters were repeatedly washed with aqueous sodium carbonate, dried and finally purified by distillation *in vacuo*. As for the other esters pure samples from Kahlbaum were available. They were however subjected to redistillation *in vacuo* before being employed for taking the Raman spectra.

TABLE I

Esters of Acetic Acid.

Benzyl acetate.	Benzyl acetate. (Morris[2]).	Phenyl acetate[1].	*Ethyl acetate.
187 (2)	..	185 (1)	..
223 (2)	..	239 (4)	..
263 (1)	..	272 (4)	..
300 (1)	..	..	..
329 (1)	364 (1)	341 (1)	376 (9)
426 (0)	..	..	..
499 (1)	479 (1)	..	..
		529 (5)	..
580 (5)	..	597 (1)	..
619 (3)	..	618 (4)	633 (9)
642 (2)	633 (1)	664 (4)	..
..	..	694 (2)	..
751 (1)	..	744 (5)	..
..	..	815 (5)	784 (3)
820 (1)	..	829 (1)	..
839 (3)	..	..	846 (10)
..	..	892 (2)	..
919 (2)	..	926 (1)	916 (1)
..	..	..	938 (1)
1002 (10)	998 (4)	1004 (10)	999 (1)
1028 (4)	1022 (2)	1027 (3)	1045 (2)
1077 (3)	..	1079 (1)	1096 (1)
1119 (3)	..	..	1114 (3)
1157 (3)	..	1163 (6)	..
1181 (2)	..	1195 (6)	..
1213 (1)	..	..	..
1244 (1)	..	..	..
1263 (2)	..	1262 (1)	..
..	..	1311 (1)	..
..	..	1369 (1)	..
..	..	1429 (1)	..
1452 (2)	..	1448 (1)	1452 (6 *b*)
1585 (2)	..	1596 (8)	..
1606 (8)	1602 (1)	..	..
1745 (4)	..	1766 (3)	1739 (6 *b*)
		2912 (3)	2880 (1)
2940 (2)	2933 (2)		2940 (9 *b*)
			2982 (7 *b*)
..	3046 (2)	..	..
3070 (7)	..	3070 (7)	..

TABLE II

Esters of Propionic Acid.

Benzyl propionate.	Phenyl propionate.	Ethyl propionate*.
184 (1)	186 (1)	..
220 (2)	230 (2)	..
263 (2)	268 (2)	..
300 (1)	..	..
329 (1)	338 (1)	376 (9)
425 (1)	..	..
495 (1)	..	..
..	529 (3)	..
580 (2)	..	..
620 (4)	618 (2)	635 (9)
640 (2)	660 (2)	..
753 (2)	740 (3)	784 (2)
824 (2)	820 (4)	..
840 (5)	..	846 (10)
..	890 (0)	..
921 (2)	926 (0)	938 (0)
1000 (10)	1004 (10)	1000 (0)
1030 (2)	1030 (2)	1045 (1)
1078 (1)	..	..
1120 (2)	..	1114 (2)
1158 (2)	1163 (3)	..
1180 (2)	1195 (3)	..
1214 (4)	..	..
1242 (2)	..	..
1264 (1)	..	..
1453 (2)	..	1452 (6 *b*)
1510 (1)	..	..
1548 (2)	1598 (6)	..
1604 (8)	..	..
1745 (5)	1760 (3)	1740 (6 *b*)
2938 (1)	2912 (1)	2940 (9 *b*)
2978 (1)	..	2982 (7 *b*)
3068 (8)	3072 (5)	..

TABLE III

Esters of Benzoic Acid.

Benzyl benzoate.	Phenyl benzoate[1].	Ethyl benzoate.
202 (2)	..	193 (3)
239 (2)	..	214 (2)
274 (2)	..	..
332 (1)	340 (3)	326 (4)
381 (1)	..	395 (1)
446 (1)	..	488 (1)
545 (1)	..	558 (1)
618 (5)	610 (3)	619 (6)
676 (3)	674 (1)	677 (4)
754 (2)	..	783 (2)
805 (1)	..	809 (2)
883 (2)	850 (2)	852 (5)
1003 (10)	1000 (10)	1004 (10)
1030 (2)	1030 (2)	1029 (3)
1111 (2)	1115 (2)	1112 (3)
1158 (2)	1158 (2)	1160 (2)
1179 (1)	1176 (1)	1178 (2)
1215 (1)	..	..
1269 (2)	1274 (3)	1277 (5)
1313 (1)	1310 (1)	1314 (2)
1378 (1)	1365 (1)	1371 (2)
..	..	1391 (2)
1451 (1)	1450 (2)	1453 (3)
1493 (1)	..	1493 (1)
1602 (10)	1604 (10)	1602 (10)
1719 (7)	1740 (7)	1720 (8)
2868 (1)	..	..
2956 (1)	2930 (1)	2935 (2)
2975 (1)	..	2972 (2)
3067 (5)	3070 (5)	3076 (6)

* These esters were investigated by earlier workers but with a view to effect a more satisfactory comparison between the various results they were reinvestigated and the results given are those obtained by the authors.

TABLE IV

Esters of Cinnamic Acid.

Benzyl cinnamate.	Phenyl cinnamate.	Ethyl cinnamate[1].
270 (1)	274 (1)	270 (1)
355 (1)	357 (1)	357 (1)
584 (1)	580 (1)	582 (1)
620 (1)	618 (1)	619 (2)
715 (2)	715 (2)	713 (2)
834 (2)	840 (2)	830 (1)
941 (2)	945 (2)	943 (2)
970 (1)	974 (2)	972 (2)
1000 (7)	1000 (7)	999 (7)
1030 (2)	1030 (3)	1030 (2)
1156 (2)	1153 (2)	1160 (3)
1182 (4)	1180 (4)	1186 (5)
1204 (6)	1202 (6)	1204 (6)
1250 (2)	1255 (2)	1250 (2)
1300 (1)	1301 (1)	1305 (1)
1452 (2)	1450 (2)	1450 (2)
1514 (1)	..	1516 (1)
1540 (2)	1540 (2)	1540 (2)
1575 (2)	1570 (2)	1578 (2)
1598 (7)	1596 (7)	1598 (7)
1634 (10)	1633 (10)	1634 (10)
1713 (5 *b*)	1742 (4 *b*)	1712 (5 *b*)
2940 (1)	2940 (1)	2940 (1)
3065 (1)	3067 (1)	3066 (1)

TABLE V

Esters of Phenyl Acetic Acid.

Phenyl ester.	Ethyl ester.
240 (1)	242 (3)
480 (1)	475 (2)
528 (1)	527 (2)
620 (3)	619 (5)
761 (2)	764 (3 *b*)
840 (1)	842 (2)
878 (1)	875 (2)
1002 (10)	1004 (10)
1030 (4)	1033 (6)
..	1108 (0)
1160 (2)	1159 (3)
1188 (2)	1193 (3 *b*)
1216 (0)	1215 (2)
..	1300 (1)
1450 (1)	1454 (2 *b*)
1582 (1)	1587 (2)
1602 (4)	1604 (6)
1761 (2 *b*)	1736 (3 *b*)
..	2875 (0)
2930 (2)	2933 (3 *b*)
2972 (2 *b*)	2972 (3 *b*)
3066 (6 *b*)	3064 (6 *b*)

Discussion of Results.—1. A comparison of the spectra of the esters of acetic and propionic acids indicates that there is a large general agreement between the phenyl and benzyl esters because of the existence in their molecules of a phenyl ring which is absent in the ethyl esters. As regards the carbonyl frequency, however, the resemblance between the ethyl and benzyl esters is very close, being much lower than that exhibited by the phenyl esters.

2. The general resemblances between the spectra of the esters of phenyl acetic, benzoic and cinnamic acids are greater since there is at least one benzene ring in all of them besides other similar structural features. Here again the carbonyl frequencies of the ethyl and benzyl esters agree closely and differ from those of the phenyl esters.

3. The Raman spectrum of ethyl propionate was studied by Kohlrausch, Koppel and Pongratz[3] who recorded the C = O frequency as 1731 ± 9 cm.$^{-1}$

Working on the same substance subsequently Paranjpe and Savanur[4] reported the C = O frequency as 1719 cm.$^{-1}$ which is much lower than the C = O frequency for benzyl propionate recorded by us and that of the ethyl esters of other aliphatic acids. Hence ethyl propionate was reinvestigated and the C = O frequency, 1740 cm.$^{-1}$, now obtained falls into line with expectations.

4. A comparison of the spectra of the esters of phenyl acetic acid with those of the corresponding esters of acetic, propionic and benzoic acids shows that the C = O frequencies in the esters of phenyl acetic acid agree closely with those given by the esters of acetic and propionic acids and are always higher than those of the esters of benzoic acid.

TABLE VI

C = O Frequencies.

	Benzyl ester.	Phenyl ester.	Ethyl ester.
Ester of acetic acid ..	1745	1766	1739
,, Propionic acid ..	1745	1760	1740
,, Phenyl acetic acid ..	..	1761	1736
,, Benzoic acid ..	1719	1740	1720
,, Cinnamic acid ..	1713	1742	1712

The above Table VI in which the results are summarised as far as the C = O frequencies are concerned shows clearly that the separation of the phenyl group from the carbonyl by a CH_2 completely prevents the transmission of the effect that was originally found to lower or enhance markedly the carbonyl frequency. The same feature can be noticed in the examples which are given in Table VII relating to other carbonyl compounds.

TABLE VII

C = O Frequencies.

Acetophenone	1679	Acetaldehyde ..	1716	Acetyl chloride ..	1798
Benzyl phenyl ketone ..	1675	Phenyl acetaldehyde ..	1718	Phenyl acetyl chloride ..	1797
Benzophenone ..	1652	Benzaldehyde ..	1700	Benzoyl chloride	1770

The results given in this series of papers indicate that the carbonyl group is readily susceptible to small changes in the structure of the molecule. It could further be concluded that the bulk and general inductive effect of adjacent groups do not have any appreciable influence as compared with the electromeric effect since a benzyl group plays the same part as an ethyl or methyl group and differs markedly from the phenyl group. The explanation obviously lies in the fact that the transmission of the electromeric effects from the benzene ring is prevented by the introduction of a CH_2 group.

Summary

Raman spectra of esters containing the benzyl group, (i) benzyl esters of various acids and (ii) esters of phenyl acetic acid derived from different alcohols, have been investigated. Data relating to other carbonyl compounds such as ketones, aldehydes and acid chlorides have been collected. In regard to its influence on the C = O frequency the benzyl group is found to resemble closely alkyl groups and to differ markedly from the phenyl. This confirms the views already expressed in Part II and establishes that the C = O group is influenced mainly by the electromeric effect. The introduction of an additional CH_2 prevents the transmission of this effect.

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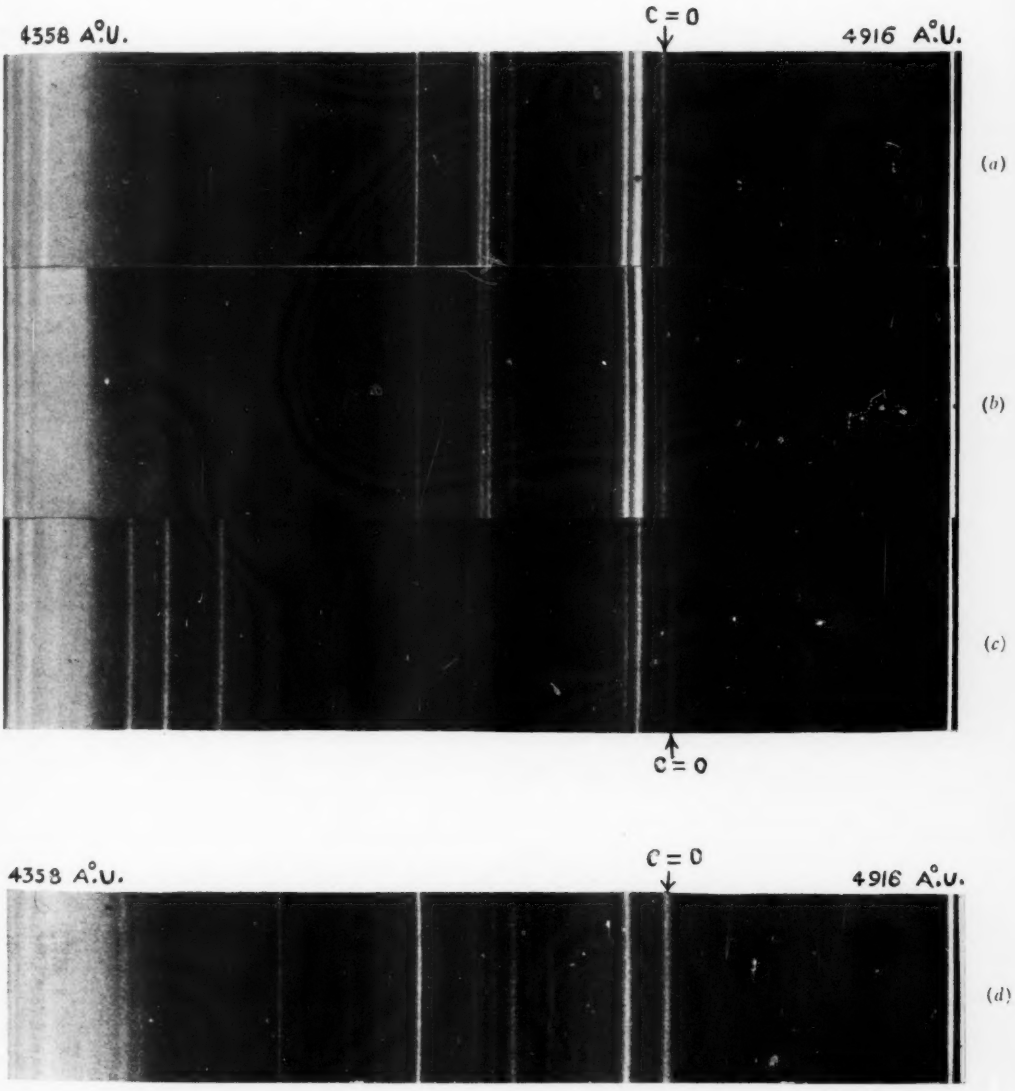

(*a*) Ethyl cinnamate (*b*) Benzyl cinnamate. (*c*) Phenyl cinnamate in carbon tetrachloride. (*d*) Benzyl benzoate.

THE DISTRIBUTION OF TEMPERATURE IN THE LOWER STRATOSPHERE

By M. W. Chiplonkar, M.Sc.

Received November 23, 1939
(Communicated by Dr. K. R. Ramanathan)

Introduction

The steady decrease of temperature with height which is the normal characteristic of the lower atmosphere, becomes small or ceases altogether at a height of about 11 km. in the temperate regions and at 16–18 km. in the tropics. Above this region of zero lapse-rate, called the tropopause, and up to a height of 25–30 km. (for which we have direct information), the temperature in the tropics increases upwards, rapidly at first and more slowly at higher levels.

While the number of sounding balloon ascents giving direct information about temperatures is fairly large up to about 20 km. it falls off at a rapid rate with further increase in height. In view of the scattered nature of the publications in which the data are available and of the fact that the persistent and characteristic rise of temperature in the lower levels of the tropical stratosphere has not yet received generally accepted explanation, it was considered desirable to collect together the available data regarding the temperatures at these heights and examine in a general way the explanations that have been put forward to account for the observed distribution of temperature.

Data Used

It was decided to include only these ascents which reached levels higher than 24 or 25 km. In the tropics, the data are mainly those of the Indian Meteorological Department. All ascents published in the departmental Upper Air Data[1] whose maximum heights were not less than 25 dynamic kilometres were picked out and their height-temperature curves plotted, separately for Agra (27° N.) and for Poona or Hyderabad (18° 32′ and 17° 25′ N.).

Even in countries of temperate latitude where the number of sounding balloon stations and the frequency of soundings are comparatively large, the

number of ascents that go up to over 25 km. is not large. Two stations in Europe for which we have a comparable number of high soundings are Lindenberg[2] and Munich[3] in Germany. At the former station, there were 11 ascents going up to 25 km. and more, between the years 1901 and 1933, and at the latter, 9 ascents between 1907 and 1934. Recently, Dr. Jaumotte of Belgium has secured a large number of high ascents at Uccle.[4] Between 1933 and 1936 he was able to obtain about 16 ascents going above 25 dynamic kilometres. An examination of British[5] and American[6] data shows that there were only 6 British ascents during the years 1922 to 1936 in which the maximum height exceeded 24 km. and 16 American ascents during the period 1904–31 reaching beyond the same limit of height. All the Indian ascents (except two which were made in the early morning) were in the late afternoon at about 17 hrs. I.S.T.; many of them were at such an hour that the sun would have set by the time that the balloons had reached the tropopause. It may therefore be accepted that these records were little affected by insolation. Of the high English ascents, all except one were made after 17 hrs. G.M.T. The German ascents were generally made in the day hours; so were all the Belgian ascents except two. The American ascents were also made in the daytime, generally in the afternoon. Although it is likely that the daytime ascents were affected by insolation, especially at the higher levels, comparison with the few available night ascents shows that the general nature of the temperature *variation* with height is not much affected although it is very probable that the actual temperatures were. The systematic difference between the temperature variation with height in the stratosphere in the temperate and polar latitudes during summer and winter, although most of the ascents in both seasons were made in the daytime, also shows that the observed variations of temperature with height can be considered to be real.

Before we discuss the distribution of temperature in and near the tropopause at different stations, it is desirable to give a small table showing the seasonal distribution of the high ascents in each place. Owing to the smallness in the number of ascents, the year has been divided into only two parts, November to April, and May to October.

General Character of the Distribution of Temperature

(1) *India* : *Agra and Poona.*—The composite height-temperature curves of Agra and Poona are shown in Figs. 1 and 2 and the mean curves in Fig. 3.

TABLE I

Place	Latitude	Number of high ascents			Remarks
		Nov. to April	May to Oct.	Whole year	
Poona (India) ..	18½°	10	0	10	Two ascents in the morning; rest after 17 hours.
Agra (India) ..	27°	12	4	16	16 to 18 hours
Avalon Groesbek (U.S.A.)	c.32°	0	4	4	Day ascents.
F. Omaha ; R. Center Huron (U.S.A.)	c.41°	1	11	12	All daytime ascents. Four ascents had abnormally high temperature near the top, probably due to insolation.
Sealand ; Kew (England)	52°	3	3	6	One ascent near mid-day, others in evening.
Ūccle (Belgium) ..	51°	2	14	16	Two ascents at night ; rest near middle of day.
München (Germany)	48°	3	6	9	
Lindenberg (Germany)	52°	0	11	11	All daytime ascents.

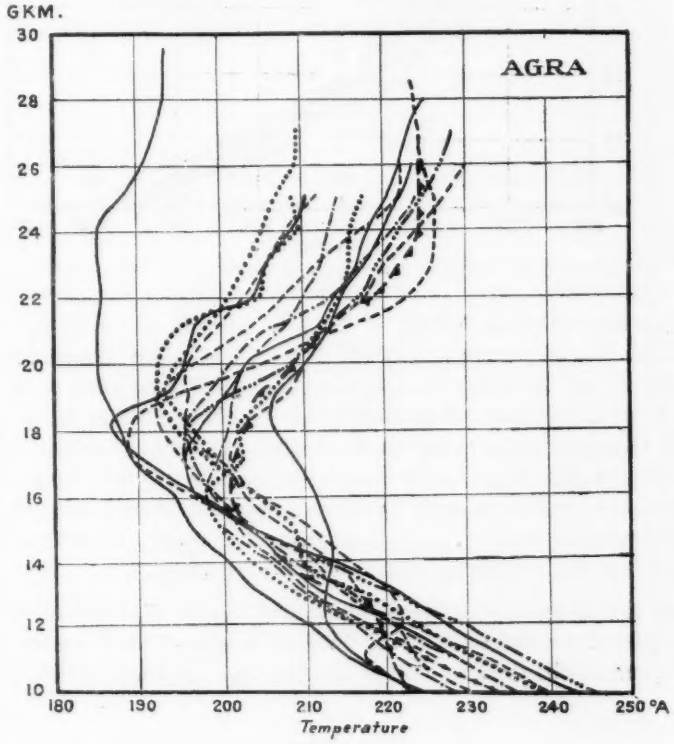

FIG. 1

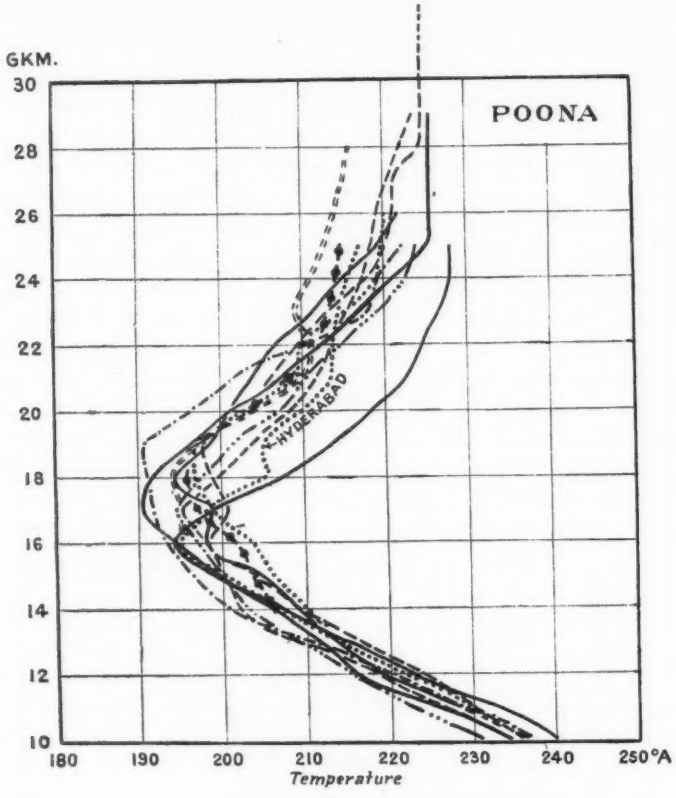

FIG. 2

The most striking feature of the low latitude curves is the large and continued rise of temperature from 18 to 25 or more dynamic kilometres. The rate of rise is largest in the neighbourhood of 21 gkm. and is on the mean 4°–5° C. per gkm. ; it gradually falls to about 2°/gkm. at 25 gkm. Of the 15 ascents at Agra going up to 25 gkm. or more, 12 ascents were made in the period November to April and the remaining four between April and October. On some occasions in winter, the Agra curves show feeble lapse rates between 12 and 17 gkm. but even on those occasions, there is invariably a rise of temperature above 18 or 19 gkm.

All the 10 ascents at Poona (including one at Hyderabad) were made in the period December to April. While the rise of temperature above 18 or 19 gkm. is observed in all the ascents, the region of feeble lapse-rates

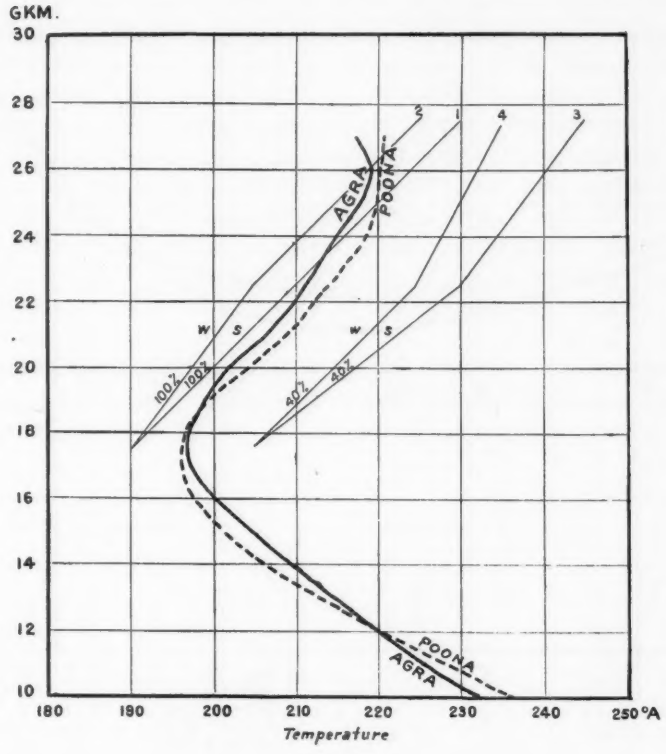

FIG. 3

Mean temperature distribution at Agra and Poona compared to the distribution calculated by Gowan for lat. 25° assuming water vapour to be mixed up in the stratosphere.

1. Summer — R.H. at tropopause = 100%
2. Winter — R.H. at tropopause = 100%
3. Summer — R.H. at tropopause = 40%
4. Winter — R.H. at tropopause = 40%

immediately below the inversion is never so thick or conspicuous at this place as at Agra. The much smaller scatter of the temperatures at Poona below 14 gkm. as compared with that above 18 gkm. is also noteworthy.

(2) *U.S.A.*—Of the 16 American ascents going up to 24 km. or more, one was in February and all the others between July and October (Fig. 4). In the United States, there were five places from which the ascents were made—Groesbek, Avalon, Fort Omaha, Royal Center and Huron—the first two being at latitudes of 31°·5 and 33°·3 N. and the other three at 40–42° N.

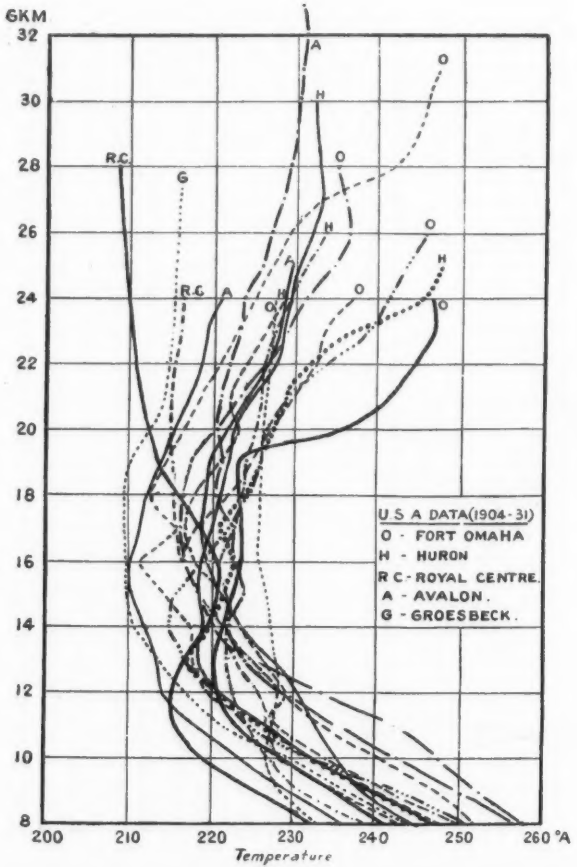
GKM
32
30
28
26
24
22
20
18
16
14
12
10
8
200
210
220
230
240
250
260 °A
Temperature
R.C.
G
A
H
O
U.S.A DATA(1904-31)
O - FORT OMAHA
H - HURON
R.C - ROYAL CENTRE.
A - AVALON.
G - GROESBECK.

FIG. 4

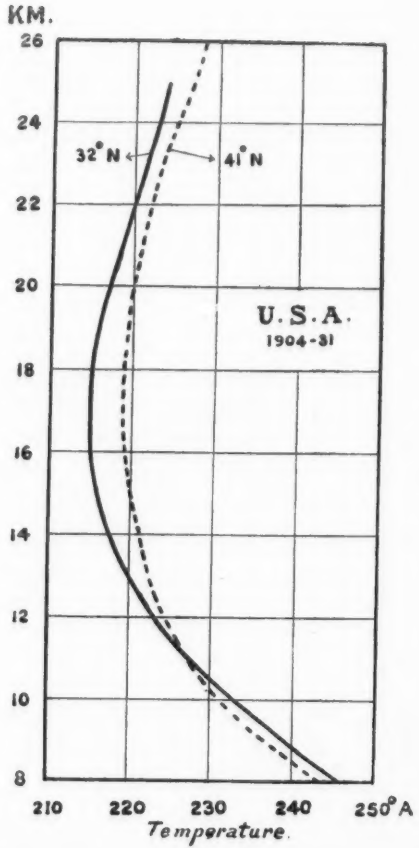
KM.
26
24
22
20
18
16
14
12
10
8
210
220
230
240
250°A
Temperature.
32° N
41° N
U.S.A.
1904-31

FIG. 5

Three of the ascents from Omaha and one from Huron show extraordinarily high temperatures near the top of their range. If we neglect these four ascents and take the means of the temperatures at Groesbek and Avalon in one group, and those at the other three stations in a second group, we obtain the mean temperatures tabulated in Table II. The composite diagram as well as the figures in the table show clearly that both at about 32° N. and 42° N., there is a continuous rise of temperature above 18 or 19 km., the rate of rise being slightly greater at the lower latitude. The American composite diagram shows that while the fall of temperature with height becomes small at 12 to 13 km. a rise of temperature with height commences in general at 18–19 km.

(3 *a*) *Europe* : (*England and Germany*).—We shall first treat the ascents at the three places, *viz.*, Lindenberg, Munich and Sealand or Kew (England). As Fig. 6 shows, the mean distribution of temperature over the three

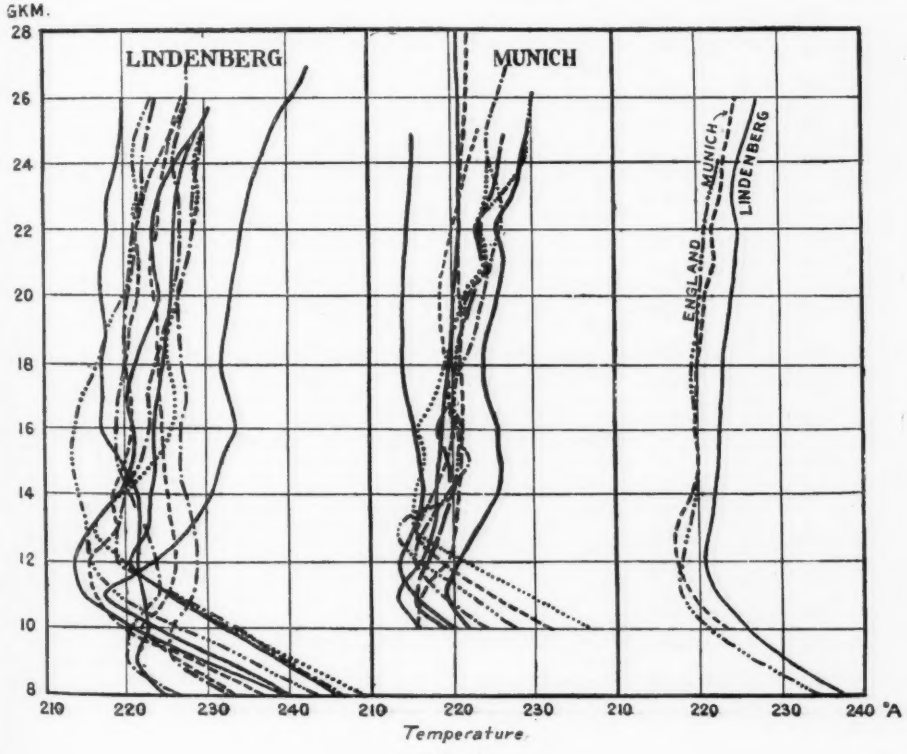

FIG. 6

places is very similar. Following an initial rise of temperature just above the tropopause and an unsteady, negligible lapse-rate upto about 17 or 18 km. there is a progressive though small rise of temperature between 18 and 24 or 25 km. Comparing the few ascents in winter with those in summer, there is hardly any rise of temperature in winter, while it is quite marked in summer.

TABLE II

Mean Temperatures and Lapse-rates

Height gkm.	Poona (Nov.—April)			Agra (all observations)			Agra (Summer)			Agra (Winter)		
	n	T	$\frac{dT}{dh}$	n	T	$\frac{dT}{dh}$	n	T	$\frac{dT}{dh}$	n	T	$\frac{dT}{dh}$
27	4	221		6	217							
			1·5			0·6						
26	6	220		9	219					8	218	
			0·6			1·2						1·2
25	10	220		15	217		4	219		11	216	
			+1·4			1·9			2·1			1·9
24	,,	218		,,	215		,,	217		,,	214	
			+2·6			2·3			2·4			2·2
23	,,	216		,,	213		,,	215		,,	212	
			+3·4			2·2			2·0			2·3
22	,,	212		,,	210		,,	213		,,	209	
			+3·4			3·8			5·6			3·2
21	,,	209		,,	207		,,	207		,,	205	
			+4·1			5·0			2·9			3·9
20	10	205		15	201		4	204		11	202	
			+5·2			2·7			3·9			2·3
19	,,	199		,,	199		,,	200		,,	198	
			+2·8			2·0			4·9			1·0
18	,,	197		,,	197		,,	196		,,	197	
			+0·6			−0·5			−1·1			−1·2
17	,,	196		,,	197		,,	197		,,	198	
			−1·1			−2·7			−2·0			−2·7
16	,,	197		14	200		,,	199		10	201	
			−4·0			−4·4			−4·4			−3·9
15	10	201		14	204		4	203		10	204	
			−4·9			−5·1			−6·6			−4·7
14	,,	206		,,	209		,,	209		,,	209	
			−6·6			−5·0			−7·1			−4·3
13	,,	213		,,	215		,,	217		,,	214	
			−7·2			−5·7			−7·5			−4·9
12	,,	220		,,	220		,,	224		,,	219	
			−8·3			−5·3			−7·6			−3·9
11	,,	228		,,	225		,,	232		,,	223	
			−7·8			−7·1			−8·0			−6·7
10	10	236		12	232		4	240		8	229	

TABLE III—(*Contd.*)

Mean Temperatures and Lapse-rates

Height km.	U.S.A. Avalon and Groesbek			U.S.A. Four stations near 41° N.			Munich (Germany)			Lindenberg (Germany)			Sealand and Kew (England)		
	n	T	$\frac{dT}{dh}$	*n*	T	$\frac{dT}{dh}$	*n*	T	$\frac{dT}{dh}$	*n*	T	$\frac{dT}{dh}$	*n*	T	$\frac{dT}{dh}$
26				5	228		4	225		7	227				
			0·7			1·5			0·5			1·3			
25	3	224		5	227		9	224		11	226		2	221	
			1·1			1·8			0·4			0·4			
24	4	223		8	225		,,	223		,,	226		6	223	
			0·8			1·3			0·5			0·6			0·9
23	,,	221		,,	223		,,	223		,,	225		,,	222	
			1·1			1·0			1·1			0·5			0·6
22	,,	220		,,	222		,,	222		,,	225		,,	221	
			1·1			1·4			−0·2			0·3			0·5
21	,,	219		,,	221		,,	222		,,	225		,,	221	
			1·8			0·9			1·1			0·5			0·2
20	4	217		8	220		9	221		11	224		6	221	
			1·3			1·0			0·5			0·6			0·8
19	,,	216		,,	219		,,	220		,,	223		,,	220	
			0·7			0·4			0·5			0·5			0·5
18	,,	215		,,	219		,,	220		,,	223		,,	219	
			− ·05			−0·3			0·2			0·1			0·3
17	,,	215		,,	219		,,	220		,,	223		,,	219	
			·05			0·4			0·1			0·2			−0·5
16	,,	215		,,	219		,,	220		,,	223		,,	220	
			−0·6			−1·5			−0·3			0·3			0·4
15	4	216		8	220		9	220		11	222		6	219	
			−0·7			−1·2			0·7			0·4			−0·2
14	,,	217		,,	221		,,	219		,,	222		,,	219	
			−2·9			−0·8			2·0			0·7			−0·4
13	,,	220		,,	222		,,	217		,,	221		,,	220	
			−3·0			−2·3			−0·1			0·6			2·2
12	,,	223		,,	224		,,	217		,,	221		,,	218	
			−4·5			−2·9			−1·7			−1·4			0
11	,,	227		,,	227		,,	219		,,	222		,,	218	
			−5·6			−4·0			−4·3			−3·6			−1·6
10	4	233		8	231		9	223		11	226		6	219	
			−6·2			−5·8						−5·3			−7·7
9	,,	239		,,	237					,,	231		,,	227	
			−6·9			−7·1						−6·6			−6·8
8	,,	246		,,	244					,,	238		,,	234	

(3 *b*) *Europe* : *Recent Belgian Ascents.*—In a recent paper,[4] Dr. Jaumotte, Director of the Royal Meteorological Institute at Ūccle in Belgium, has discussed the results of a number of sounding balloon ascents made at Ūccle during 1933 to 1936, some of them going up to 30 km. There were in all 16 ascents going above 25 dyn. km. Jaumotte had found the systematic existence of an inversion of temperature in the stratosphere over Ūccle—generally commencing at some level between 15 and 18 km. in the summer and autumn of 1933. He had attributed this to the pollution of the upper atmosphere by matter thrown up from a volcanic eruption in the Cordilleras in April 1932.

Later work by Jaumotte himself in 1934, 1935 and 1936 showed that the stratospheric inversion appears every year systematically in spring and disappears in winter. The increase is rapid in May, and maximum values of inversion are reached in June–July.

Most of the Jaumotte's ascents were made during the daytime, near about noon. There were however a few night ascents—which showed the same phenomenon.

General Summary of Facts

The rise of temperature with height between 18 and 25 gkm. is a permanent feature of the tropical stratosphere. In winter over Agra, the lapse-rate sometimes becomes small between 12–13 and 18 gkm., but this does not affect the rise of temperature above 18 km. In temperate latitudes, the region of weak lapse-rates begins at a lower level and is present throughout the year but even in these latitudes there is a persistent, though weaker rise of temperature with height above 18 or 20 gkm. in summer ; in winter, this rise of temperature is generally not evident. In the polar regions where the temperature distribution has been recently studied by soundings by Rolf[7] at Abisko and I. G. Gutermann[8] in Franz Joseph Land, there is a large seasonal variation of temperature in the stratosphere, the months of maximum and minimum temperatures coinciding with those of maximum and minimum altitudes of the sun. In polar regions in summer, there is a rise of temperature with height between 12–13 and 19 km., while in winter, there is a gradual fall with height.

In Fig. 7 are shown the mean temperatures at different levels in summer and winter over Munich ($\lambda = 48° 10'$), Abisko ($\lambda = 68° 18'$) and Franz Joseph Land ($\lambda = 81°$). In all the three places, the nature of the temperature variation with height is similar in both the seasons, but the annual amplitude of temperature is a maximum near the pole and decreases with decrease of

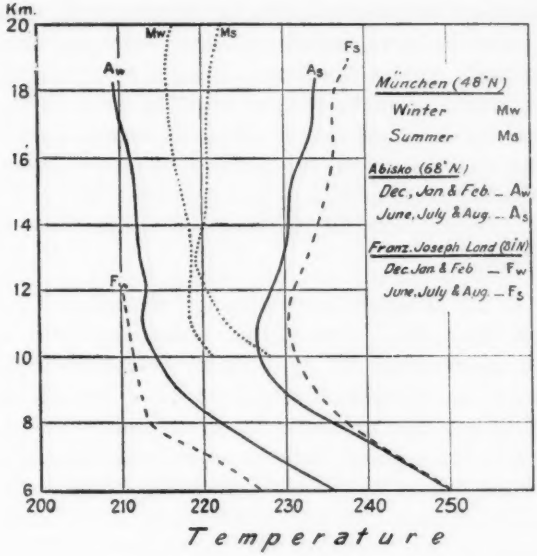

FIG. 7

latitude. It will also be noticed that in all the places the amplitude increases with increase of height in the stratosphere.

Discussion

The classical theory of the radiation equilibrium[9] of the stratosphere, which is associated with the names of Gold, Humphreys, Emden and others and which takes account only of the long-wave radiation and absorption having its origin either on the surface of the earth or in the water-vapour contained in the atmosphere, shows that above a level where the pressure is one-fourth the surface pressure, the absorption and emission will on the whole balance each other. But within this region of radiation equilibrium, the lower half will be slightly heated and the upper half cooled. The net effect of long-wave radiation and absorption will, therefore, be to produce a slow fall of temperature with height. If a part of the incoming solar radiation is also absorbed by the water-vapour or some constituent of the atmosphere which has a similar distribution as water-vapour, then, given a suitable mean coefficient of absorption for solar radiation, it is possible to have a high boundary temperature in the stratosphere for low angles of the sun. But it does not appear that water-vapour has such a convenient coefficient of absorption for solar radiation.

The rise of temperature with height in the stratosphere over the tropics and sub-tropics and the large annual variation of temperature in the stratosphere over the polar regions can be explained if an appreciable fraction of the short-wave radiation of the sun is absorbed at such low heights as 20 km. The recent measurements of Götz, Meetham and Dobson, and of Regener showing that the centre of gravity of the ozone layer in the atmosphere may be as low as 20 or 22 km. lend support to the view that the presence of ozone is responsible for the observed temperature distribution in the lower stratosphere.

Recently, E. H. Gowan[10] has examined the effect of ozone on the temperature of the upper atmosphere. Assuming that the centre of gravity of the ozone layer is at 22 km., Gowan has calculated the mean temperatures in different layers from 11 to 50 km. under several assumptions regarding the amounts of ozone and water-vapour and its distribution in the stratosphere. The assumptions as regards water-vapour include those of 100% humidity and 40% humidity at the base of the stratosphere and either diffusion in the stratosphere according to molecular weight or mixture with air so that the vapour pressure is proportional to total pressure. Under permanent night conditions, the calculations show only a small rise of temperature from 20–25 km. to 40 km. and a small fall thereafter, but under day conditions, a large rise of temperature from 15–20 km. to 40–45 km. is shown, the amount of rise depending on the assumptions as regards ozone and water vapour content and their distribution. The observations over Agra agree fairly well with the calculations made on assumptions that at the tropopause the atmosphere is saturated with water-vapour and that the vapour is mixed up with the air in the stratosphere in the proportion in which it is present at the tropopause (see Fig. 3).

Penndorf has calculated the rate of rise of temperature in different layers due to absorption of solar radiation and absorption and radiation of long-wave radiation. He says: "Comparing the effect of long- and short-wave radiation, we find that the net loss of heat by nocturnal radiation is balanced* by the net gain of heat absorbed from the solar energy, and that the energy gained is at least 10 times more than that lost. In summer the difference is about 60 times.

* By 'balanced,' the author apparently means 'compensated' or 'more than compensated'.

The resulting effect of this heat reservoir must be that the temperature of the stratosphere cannot remain constant with increasing height. The ozone layer gives rise to a marked increase in temperature. Moreover, the height of the maximum is in fairly good accordance with other geophysical effects which demand high temperatures in the level of about 50 km."

From the available evidence, it is very probable that the rise of temperature above 18 km. observed in the tropics is due to ozone. Jaumotte expresses a similar view with regard to the rise of temperature observed by him over Brussels in spring and summer. The greater rate of rise over the tropics than over temperate latitudes is probably due to the fact that the temperature of the tropopause in low latitudes has been lowered much below the radiation equilibrium temperature due to the effect of convection from below. The fact that the height of the tropopause increases owing to increased convection is shown by the occurrence of the maximum height of the tropopause over Agra during the monsoon. But, as pointed out by Ramanathan in his paper on Agra soundings, when we plot the height of the tropopause against its temperature, the height does not increase appreciably when the temperature falls below 200 Å.

There is apparently a strong force resisting the raising of the top of the troposphere.

There are in general two levels where changes of lapse-rate occur ; one where mixing up practically ceases and approximate radiation equilibrium due to water-vapour commences, and another where rise of temperature due to absorption of solar radiation by ozone begins. In the tropics, the two practically coincide and in the temperate regions they separate out, one getting lower and lower and the other remaining steady or slowly rising.

My thanks are due to Dr. K. R. Ramanathan for his kind interest in the work and to the Director-General of Observatories, Poona, for allowing me the use of the library facilities of the India Meteorological Department.

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RAMAN SPECTRUM AND MOLECULAR ASSOCIATION IN FORMAMIDE

By Bishambhar Dayal Saksena

(From the Department of Physics, Indian Institute of Science, Bangalore)

Received December 12, 1939

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

The physical properties of formamide are in many respects similar to those of water ; but, though the Raman effect investigations on water are legion, formamide appears to be very insufficiently studied in the Raman effect and infra-red. Besides being solvents, both substances possess a high dielectric constant, a unique dissociating power (Walden), and a high degree of association (Ramsay and Shields). It is well known that ice is tetra-co-ordinated H_2O. The high melting and boiling points of amides have long been recognised as evidence of a high degree of association. According to Turner (1910) and Getman (1936) the association factor is 6 and it decreases rapidly with temperature. Smith (1931) measured the parachor values between 18° and 50° C. and found that they increase steadily with the rise of temperature, being 109·6 at 18° C. and 111 at 50° C., the calculated value of the parachor for a single molecule being 111·8. To explain the association factor of 6, Walden put forward a molecular model of a six-membered ring of $C\begin{matrix}OH\\ \diagdown\\ \diagup\\ NH_2\end{matrix}$ groups, but the parachor measurements do not support the idea. Herzberg and Köloch (1933) using ultra-violet excitation have reported that the vapour of formamide shows no absorption characteristic of N − H or C = O. Copley, Zellhoefer and Marvel (1938) from the extremely low solubility of mono-fluoro-dichloromethane in formamide have suggested the formation of large polymers which may have a linear structure or a fused dimer type of structure. Buswell and Rodebush (1938) from the infra-red study of amides come to the conclusion that amides show a strong tendency towards association. According to these authors unsubstituted amides do not form dimers, but if they do they have no tendency to enolise. But certain reactions of amides, *e.g.*, alkylation, indicate that amides may have tautomeric structures $R-\overset{OH}{\overset{|}{C}}=NH$ and $R-\overset{O}{\overset{\|}{C}}-NH_2$. Kumler and Porter (1934) have measured the dipole moment of $CH_3-\overset{OC_2H_5}{\overset{|}{C}}=NH$ and

have shown that the value deduced for the enolic form of acetamide $CH_3—\overset{OH}{\overset{|}{C}}=NH$ is much smaller than that observed for acetamide, thus showing that the proportion of tautomer molecules of acetamide should be very small. The structure of amides is still an open question. The present paper aims at a study of the association in formamide by means of the Raman effect. With this view the Raman spectrum of formamide was studied at various dilutions and temperatures and a polarisation study of the Raman lines was also made.

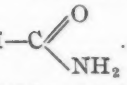
2. *Results*

The Raman spectrum of pure formamide was obtained by the author by (1) using both excitations and (2) by cutting off 4358 excitation with a filter of iodine in carbon tetrachloride and of its solutions in water, by cutting off the 4046 excitation with a sodium nitrite filter. The effect of temperature was studied by using both excitations. All the observations were made on a Fuess glass spectrograph but to test the presence of low frequency lines some exposures were also made on a Hilger two-prism glass spectrograph. The polarisation of the Raman lines was studied in the usual way by passing the scattered beam through a double-image prism. The results are tabulated in the following table, the state of polarisation of the lines is indicated by letters P and D—P polarised, D depolarised.

The Raman spectrum of formamide has been previously investigated by Kohlrausch and Pongratz (1934) and Thatte and Joglekar (1935). The results of the latter are very incomplete and are therefore not included in the table. The frequencies reported by Kohlrausch and Pongratz are given in column (1). The line 1005 ($\frac{1}{2}$) recorded by these workers is in fact $k \rightarrow 2772$ because it is not obtained when sodium nitrite is used as filter, and with 4046 excitation the frequencies at 2695 (diff.) and 2766 are distinctly recorded. In a very recent publication (July 1939) Rietz and Wagner have confirmed the earlier work of Kohlrausch and Pongratz with the addition of two new lines at 507 and 691 and a band extending from 3122 to 3460. The author has been unable to report the line 507 because with 4358 excitation the line does not come out, and with 4046 excitation the line $k \rightarrow 507$ is most likely $p \rightarrow 3176$ ($p = 27353$ cm.$^{-1}$).

Kohlrausch and Pongratz	Author Temp. 25° C. both excitations	Author Temp. 25° C. 4046 excitation	Author State of polarisation	Author Temp. 144° C. both excitations	Author Concentration in H_2O −50% 4358 excitation	Author Concentration in H_2O −25% 4350 excitation	Remarks about changes in the nature of the lines on dilution
	200 (3) *br*	..	D				
608 (4)	603 (2) 700 (0) 780 (0)	603 (4)	*w.* P	603 (2)	605 (2)	605 (2)	
1005 ($\frac{1}{2}$)	..	..					
1050 (1)	1048 (0)	1051 (2)	D	1049 (1)	1053 (1)	1051 (1)	
1094 (2) *br*	1095 (2) *br*	1094 (7) *br*	P	1098 (2)	1092 (2)	1090 (2)	
1314 (6)	1309 (5) *v. br*	1309 (10) *v. br*	P	1302 (5)	1321 (7)	1326 (7)	becomes sharper
..	..	1341 (2) *s*	P	..	1346 (2)	1346 (3)	becomes stronger
1390 (10) *s*	1391 (10) *s*	1391 (15) *s*	P	1394 (10)	1390 (10)	1388 (10)	
1599 ($\frac{1}{2}$)	1591 (1) *di*	1594 (2)	P	1606 (1)	1601 (2)	1596 (2)	becomes sharper.
1672 ± 11 (2)	1672 (2)	*i*-1672 (1) 2008 (0) 2083 (1) 2695 (0) *diff.*	P	1678 (2) *br*	1683 (3) *br*	1683 (3) *br*	is asymmertic and broad in pure substance and becomes sharper.
	2766 (1)	2766 (3)	P				
2882 (8) *br*	2885 (8) *br*	2889 (12)	P	2889 (8) *br*	2889 (8)	2889 (8)	
		3176 (4) ↓					(N–H) band extending from 3176 to 3480 with three maxima at 3176, 3265 and 3338 cm.$^{-1}$
3347 (1)		3265 (1) ↓					
3376 (1)		3338 (2) ↓					
v.w.		3480					

3. Discussion of Frequencies

The structure of formamide can be represented by the formula  . It can also be considered as an aldehyde $NH_2 \cdot CHO$. Kohlrausch has shown that the frequency 1390 appears in nearly all the aldehydes with the exception of formaldehyde $H \cdot CHO$, and Kohlrausch regards this line as a HCO deformation frequency. This line appears in formamide $NH_2 \cdot CHO$ and also in formic acid $OH \cdot CHO$ as a sharp line with nearly unchanged frequency. The line 2886 in formamide is the C–H frequency, the C–H frequency in formic acid being 2962. As the masses of NH_2 and OH groups are nearly the same and further as the C–N and C – O force constants are also nearly the same, the lowering of the C–H frequency in formamide may not be due to constitutive influences alone but also due to association. The lines 2766 and 2695 may be considered as independent C–H frequencies or as overtones and combinations thus:

$$2766 \sim 2 \times 1390, \qquad 2695 = 1390 + 1309.$$

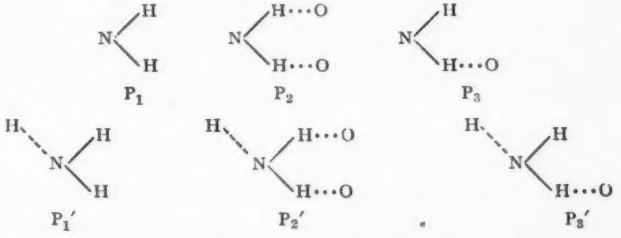
The question is difficult to decide because both the C–H frequency and the overtones are and should be polarised. Formic acid [Edsall (1935)] also gives two similar lines 2778 and 2592, the latter being very weak. Considering NH_2 as one group the molecule will have six vibration frequencies; of these five planar ones are polarised, and the one perpendicular to the plane is depolarised. Of these two polarised vibrations 1390 and 2886 have already been considered. The remaining polarised vibrations include the C = O frequency occurring at 1672 and other vibrations 1342 and 603. It appears probable that 1342 is a monomer frequency because it gets stronger as dilution progresses. The depolarised vibration occurs at 1050. The same frequency also occurs in formic acid and is also depolarised. The group NH_2 will have three N–H frequencies, two of the valence type and the other a deformation. The N–H frequencies fall in the region 3330 and one of the valence frequencies may be identified with the line 3338; the δ (N–H) falls in the region 1600. Both these lines should be polarised. The weak intensity and diffuse nature of the polarised line 1600 suggests that it is a δ (N–H) oscillation. There are still several lines left unexplained: 3265, 3176, 1309, 1090, 780, 700, 200. The lowering of N–H frequency to 3265, 3176 may be due to association, and similarly the low frequency band at 200 may be due to formation of polymers. The formation of polymers is also suggested by the fact that all the lines excepting 1051 and 200 are polarised. All the amides show this lowering in their C = O and N–H frequencies.

Formamide	1600 (1)	1672 ±11	3176 (4)	3265 (1)	3338 (2)
Acetamide	1611 (2)	1660± 9	3150 (6)	3286 (1)	3354 (4)
Propionamide	1603 (2)	1664 ±13	3173 (4)		3356 (3)
Butarimide	1582 (2)	1673 (2)	3167	3262	3325

Acetamide and propionamide have been examined by Ananthakrishnan (1937) in the solid state and by Kohlrausch and Pongratz (1934) in the molten state, Butarimide has been examined by Rietz and Wagner (July 1939). As the N–H and C = O frequencies are not appreciably different in different amides, it follows that association in all these amides is of the same type. According to Rodebush and Buswell, propionamide shows three infra-red bands for the N–H region—one at 3·15 μ (3175 cm.$^{-1}$), which is considerably influenced by dilution and two others which occur at 2·83 μ (3533) and 2·92 μ (3424). The last two are considered by these authors as the valence N–H frequencies.

4. *Width of the N–H Band*

Cross, Burnham and Leighton (1937) have explained the width of water bands on the basis of various co-ordinations present in the water molecule on account of hydrogen bonding. The effect of hydrogen bonding is a sort of perturbation and this leads to a sequence of frequencies different from the original valence frequencies of the H_2O molecule. The Raman and the infra-red bands are merely the envelopes of these frequencies. The NH_2 group presents six possibilities of co-ordination if we assume that the nitrogen of one molecule forms a hydrogen bond with the C–H group of another; such association linkages have been considered by Zellhoefer, Copley and Marvel (1938). These are :



ν_σ and ν_π, the valence N–H frequencies, may be taken as 3424 and 3338 respectively; the former comes out strongly in the infra-red and the latter

strongly in the Raman effect. Regarding these two frequencies as a result of coupling of two N–H oscillators of frequency ν_0 so that $\nu_\sigma = \nu_0 + \epsilon$ and $\nu_\pi = \nu_0 - \epsilon$, we have $\epsilon = 43$, $\nu_0 = 3381$. Further, if δ represents the diminution in frequency due to the linking of nitrogen to the hydrogen atom of another molecule and Δ the diminution in frequency due to the linking of the hydrogen of the NH_2 group to the oxygen of another molecule, one gets, considering the line 3173 as the N–H frequency corresponding to complete co-ordination, $\Delta = 120$, $\delta = 45$.

	ν_σ	ν_π	ν_σ	ν_π
P_1	$\nu_0 + \epsilon$	$\nu_0 - \epsilon$	3424 (1)	3338 (1)
P_1'	$\nu_0 - \delta + \epsilon$	$\nu_0 - \delta - \epsilon$	3379 (1)	3293 (1)
P_2	$\nu_0 - \Delta + \epsilon$	$\nu_0 - \Delta - \epsilon$	3304 (1)	3218 (1)
P_2'	$\nu_0 - \Delta - \delta + \epsilon$	$\nu_0 - \Delta - \delta - \epsilon$	3259 (1)	3173 (1)
P_3	$\nu_0 + \frac{\epsilon^2}{\Delta}$	$\nu_0 - \Delta + \frac{\epsilon^2}{\Delta}$	3395 (·2)	3271 (·8)
P_3'	$\nu_0 - \delta + \frac{\epsilon^2}{\Delta}$	$\nu_0 - \Delta - \delta + \frac{\epsilon^2}{\Delta}$	3340 (·2)	3206 (·8)

ν_π frequencies are Raman-active for classes P_1 to P_2' and for classes P_3 and P_3' both ν_σ and ν_π are Raman-active. It is seen that N–H frequencies extend out into a band of nearly equal intensity extending from 3173 to 3395. The calculated intensities of the lines or bands are shown in brackets. The observed band extends from 3173 to 3480 with three maxima at 3176, 3265 and 3338. The observed intensity of these maxima shows that molecules exist largely in the state P_2', some in the monomer state P_1, while a much smaller number exists in the dimer state P_3. This conclusion is borne out by the polarisation results according to which almost all the lines are partially polarised. Further, as already stated, the presence of the monomer molecule is exhibited by the line 3338 and by the depolarised line 1051.

5. *Effect of Temperature*

The effect of temperature on the frequencies is not marked. Pictures were taken at several temperatures but at 144° a noticeable change was ecorded in the line 1309 which shifted to 1302. The C = O frequency hows no change in the frequency and in its outward appearance. This

indicates that molecules are still polymers, but it is significant that the change in frequency in the line 1309 brought about by the increase of temperature is opposite to the change produced by dilution. It may be that more significant changes may be expected at higher temperatures but at about 200°C. the pure substance became yellow and highly fluorescent. Probably it is highly photo-sensitive at this temperature.

6. *Effect of Dilution*

There are marked changes on dilution :

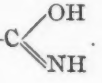
(1) The line 1309 of pure substance shifts to 1326 at 25% dilution and becomes sharper.

(2) The sharp line 1341 which is very weak in the spectrum of the pure substance becomes stronger as dilution progresses.

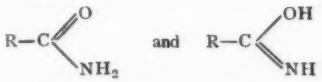
(3) The line 1672 is broad with a sharp edge towards the exciting line and has an intensity maximum at the edge. At 25% dilution, the intensity maximum has shifted towards the side of longer wavelength and there is a shift of about 10 $cm.^{-1}$ The line becomes sharper on dilution.

(4) The line 1599 which is diffuse for pure substance becomes sharper.

(5) The sharp line 1390 shows a shift of about 6 $cm.^{-1}$ at 25% dilution.

Getman (1936) has reported that solutions of formamide in water behave as if both the liquids have become less associated. The sharpening of most of the lines on dilution lends support to this view. The line 1309 is very much influenced by the effect of temperature and dilution, but the line 1051 and 1090 are unaffected. The lines 1090, 1309, 1599 and 1672, 2886 are all broad, perhaps the breadth of the lines is due to association. It also appears significant that the lines 1090, 1309, 1672 have fainter companions 1051, 1342 and 1599. By analogy with formic acid where we have two C = O frequencies 1728 and 1672, 1728 representing monomer molecules, and 1672 dimer molecules, Reitz and Wagner (1939) conclude that 1672 in formamide represents monomers and 1599 represents dimers. But the analogy does not hold good because in formic acid 1728 is depolarised, and 1672 polarised, whereas in formamide both lines 1672 and 1599 are polarised. If we regard 1599 as a δ (N–H) frequency, then the sharpening of the line on dilution can be understood because the N–H frequencies take part in association. According to Kohlrausch the line 1600 represents molecules of type  . It is very difficult to say whether molecules with

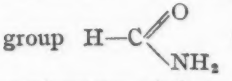
alternative structures of type

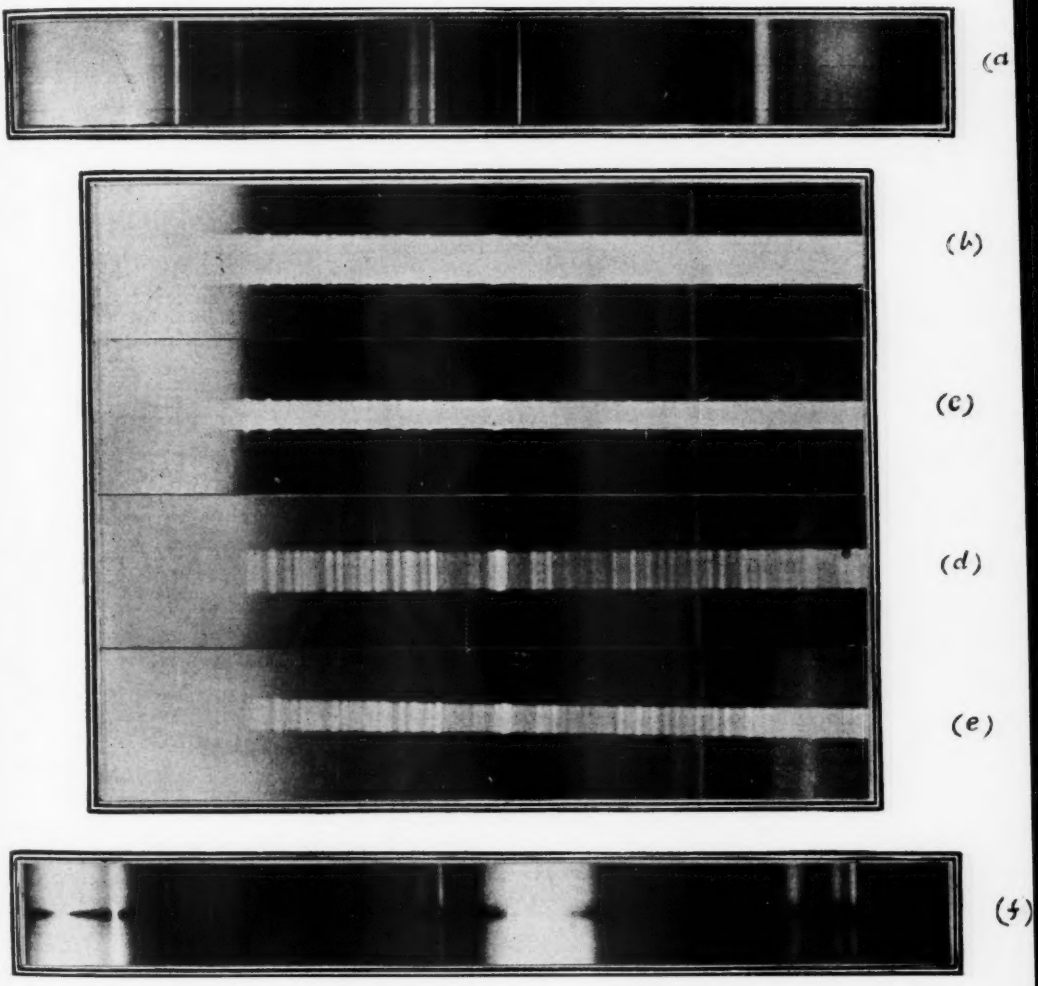


co-exist. The occurrence in pairs of the lines 1091, 1309 and 1672 may or may not be due to this cause. However polarisation and other results show definitely that the molecules in formamide exist largely as polymers and to some extent as monomers.

In conclusion, the author thanks Professor Sir C. V. Raman for his kind interest in the work.

7. *Summary*

The Raman spectrum of formamide has been investigated in the pure state and at various dilutions and temperatures. A polarisation study of the Raman lines has also been made. Several new lines 200, 780, 1342, 2008, 2083, 2695, 3176, 3265 have been observed for the pure substance. At 144°, the line 1309 of the pure substance shifts to 1302, and this is the only change observed with the increase of temperature. Marked changes in the lines are observed on dilution (1) the line 1309 shifts to 1326 at 25% dilution and becomes sharper; (2) the sharp line 1341 becomes stronger; (3) the line 1599 becomes sharper; (4) the line 1672 which is broad with a sharp edge having maximum intensity towards the exciting line becomes sharper and more symmetric, and shows a shift of about 10 cm.$^{-1}$; and (5) the sharp line 1390 shows a shift of about 6 cm.$^{-1}$ at 25% dilution. The polarisation results show that all the lines are polarised excepting 200 and 1051. The frequencies have been classified as six frequencies of the group  taking NH_2 as one group. Further, following the explanation of Cross, Burnham and Leighton for the width of water bands, it has been shown that N–H frequencies should spread into a band on account of the six possibilities of co-ordination existing for the NH_2 group. The N–H band extends from 3176 to 3480 with three intensity maxima at 3176, 3265, 3338. The line 3176 represents polymer molecules with maximum co-ordination and the line 3338 monomer molecules. These ideas are supported by polarisation results because the line 3338 and the depolarised line 1051 represent monomer molecules. As nearly all the lines are partially polarised, it follows that the molecules are largely polymers with some small percentage of monomers as well.



Raman spectra of formamide

(*a*) of pure substance with 4046 excitation only; (*b*) of pure substance at 25°C. with both excitations; (*c*) of pure substance at 144° C. with both excitations; (*d*) of 50% solution in water using $NaNO_2$ filter; (*e*) of 25% solution in water with $NaNO_2$ filter; (*f*) state of polarisation of Raman lines in pure substance.

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EFFECT OF CRYSTAL ORIENTATION ON THE RAMAN SPECTRUM OF CALCITE

By S. Bhagavantam

(From the Department of Physics, Andhra University, Waltair)

Received January 3, 1940

1. Introduction

Much of the experimental work so far done in the subject of Raman effect relates to either the liquid or gaseous states of matter or crystals in the form of powders. It is easily seen that the scattering unit cannot be regarded as having a definite orientation in any of these cases. On the contrary, in most of the above cases, the opposite extreme is reached as we are obliged to postulate a completely random orientation in order to interpret the observed results as average effects. This defect can only be remedied by using a suitably cut single crystal and studying the nature of the scattered light for different orientations of the crystal. Corresponding to each possible orientation of the crystal, the state of polarisation of the incident light may also be varied and such studies will undoubtedly reveal a wealth of information which was hitherto missed. The importance of obtaining such results has been stressed elsewhere.[1] The work that has so far been done on these lines is however very meagre. Reference may be made to Schæfer, Matossi and Aderhold,[2] Miss Osborne,[3] Cabannes and Canals[4] and Michalke.[5] All these authors obtained some results with calcite but unpolarised incident light was generally used. Only Miss Osborne employed linearly polarised as well as unpolarised incident light and studied the case of calcite in great detail. The agreement between the results obtained by the various authors is not very satisfactory. These features have been briefly reviewed by Nedungadi[6] in a recent publication. Nedungadi has also pointed out that the nitrates and carbonates form very favourable material for such studies and he himself has described in great detail the results obtained with $NaNO_3$ crystals. In the present investigation, the Raman spectrum of calcite which resembles that of $NaNO_3$ in many respects has been similarly studied.* The resemblance between the two cases is in fact so close that it very often becomes unnecessary to distinguish between them. The Raman spectra of these two crystals, without reference to directional excitation, have recently been studied in this laboratory by Sundara Rama Rao[7] and a reference to this

* A preliminary note (*Curr. Sci.*, 1939, **8**, 507) by the author contains some of the results of this paper.

paper will facilitate proper appreciation of the results which will be described in the following sections.

2. *Experimental Arrangements*

A one-inch cube of calcite cut in such a manner that the optic axis is parallel to one of its edges is used for obtaining the Raman spectra reproduced in Plate III. All the faces of the cube are polished. We shall designate the direction of incident light by OX and the direction of scattered light by OY. The three edges of the crystal are always along OX, OY and OZ. This notation as well as the notation that will be employed in the rest of the paper and the description of the figures in Plate III are deliberately so chosen that they conform closely to the descriptions already used by Nedungadi in order to avoid confusion. In the experimental arrangements, suitable apertures designed to minimise parasitic light are provided at appropriate places. Light from a quartz mercury lamp is focussed on the crystal by a large glass condenser involving a semi-angle of convergence of about 10°. It is found impracticable to eliminate the convergence altogether and this should at present be regarded as an inevitable defect of the experimental arrangements. A suitably oriented Polaroid disc is used for securing the desired state of polarisation for the incident light. The scattered light is separated into the horizontal and vertical components by means of a double-image prism and the two components are simultaneously photographed on Golden Iso-Zenith plates using a high light gathering power 2-prism glass spectrograph. λ 4358 is the exciting radiation. In all cases, graded intensity marks are given by the method of varying slit widths and wherever necessary, figures relating to the intensities are obtained from the density-log intensity curves. In other cases, where such an accurate study is not called for, either because the lines under comparison possess very widely different intensities or because the intensities are so small as to fall within the limits of convergence errors, only visual estimates are given. These figures are collected together in Table I. An arbitrary intensity of 100 is assigned to the strongest line in each plate and the intensities of all other lines are expressed in relation to this figure. The observed polarisation ratios are corrected for the errors introduced by oblique refraction at the surfaces of the prisms.

3. *Results*

Nedungadi has shown that 27 different spectrograms may be obtained for the case of transverse scattering with uniaxial crystals but it may easily be seen that 12 of these are the most important ones. These have been given as Figs. 4, 5 and 6 in his paper and correspond in the same order to Figs. 1, 2 and 3 of this paper. As has been done by Nedungadi, the directions

TABLE I

Serial number	Direction of vibration of incident light along	Orientation of the optic axis along	Relative Intensities of Components of Raman lines											
			155		282		709		1084		1434		1749 (overtone)	
			OX	OZ	OX	OZ	OX	OZ	OX	OZ	OX	OZ	OX	OZ
1	OZ	OX	25	1	60	2	10	5	5	100	2	..	..	2
2	OY	,,	50	..	100	..	2	..	2	5	..	..	..	..
3	OZ	OY	5	5	10	10	10	10	60	100	3	3	2	2
4	OY	,,	50	50	100	100	3	3	20	10	..	..	..	..
5	OZ	OZ	50	0	100	3	..	..	5	10	..	..	..	..
6	OY	,,	25	50	50	100	20	..	50	5	5	..	..	..

of the vibrations in the incident light (I.L.) as also those in the scattered light (S.L.) are indicated in the figures. Vibrations along OX and OY are represented by arrows parallel to these axes, whereas a circle with a central dot indicates that the vibrations are along OZ. The orientation of the CO_3 ion and therefore the crystal as a whole adopted in each case is also indicated by the side of the corresponding set of pictures. Results of visual estimate and quantitative measurement are contained in Table I. This corresponds to Table III of Nedungadi's paper.

A very satisfactory agreement between the general run of figures, in Table I and the results obtained by Nedungadi may be noticed. The following main conclusions may now be drawn from the results in Table I and the pictures reproduced in Plate III.

On comparing Figs. 1, 2 and 3, taking *a* and *b* components together in each case, it will be seen that the 1084 line is very weak in Fig. 3 while it is quite strong in Figs. 1 and 2. In all these cases, the incident light is polarised in the same way but the orientation of the crystal is different. This implies that the change of polarisability of the CO_3 ion due to its total symmetric oscillation is much smaller when the incident light vector is perpendicular to the plane of the ion than when it is parallel to it. The lines of frequency shifts 709 and 1434 due to the two degenerate internal oscillations of the CO_3 ion also appear to behave in a similar manner but the differences are less prominent. Similar results have been obtained by Nedungadi with $NaNO_3$.

On comparing *a* and *b* taken together of Fig. 2 with *c* and *d* of the same figure taken together, it is seen that while the low frequency lines are weak and the internal oscillations are strong in the former case, the reverse is the situation in the latter. Similar results have been obtained by Nedungadi with $NaNO_3$. It may be concluded from this result as has been done by Nedungadi that the behaviour of the two kinds of oscillations, namely the low frequency ones on the one hand and the internal oscillations on the other, is reciprocal in character and that the periodic changes of polarisation responsible for the former arise in a manner fundamentally different from that operative in the case of the latter.

The behaviour of the 155 and 282 lines is closely analogous. A reversal of relative intensities amongst these two lattice oscillations noticed by Nedungadi in $NaNO_3$ for a particular orientation (Fig. 6 *c* of his paper) is not confirmed by the author in $CaCO_3$ as may be seen from Fig. 3 *c* which is the corresponding figure in this paper.

The first overtone of a Raman inactive frequency (879) is recorded at 1749 in two cases and it may be noted that in both these cases, its behaviour is similar to that of the total symmetric oscillation at 1084 (see Table I).

Figs. 1 (*a* and *b*) and 2 (*a* and *b*) show that the polarisation characters of the two low frequency lines are similar to those exhibited by the degenerate internal frequencies at 709 and 1434 and opposite of those exhibited by the total symmetric oscillation at 1084. In Fig. 3 (*c* and *d*) the reciprocal behaviour of the low frequency lines on the one hand and the 1084 line on the other persists but the internal degenerate frequencies in this case appear to resemble 1084 and not the low frequency lines. Some of these results are not in conformity with those obtained by Nedungadi in $NaNO_3$.

4. Comparison of the Results with Earlier Observations

It has already been pointed out that Miss Osborne had obtained some results with calcite utilising plane polarised incident light. These results which refer to the state of polarisation of the Raman lines are compared below in Table II with the values obtained in the present investigation. Excessively large values are denoted by ∞ and excessively small ones by 0. The serial number in Table II corresponds to that given in Table I and determines the crystal orientation. O stands for Miss Osborne and B for the author. *f* denotes that the line fails to appear.

TABLE II

Serial number	ρ for 282		ρ for 709		ρ for 1084	
	O	B	O	B	O	B
1	4	∞	1	>1	0	0
2	4	∞	1	>1	0	<1
3	1	1	1	1	1	<1
4	1	1	*f*	1	*f*	>1
5	>1	∞	>1	..	0	<1
6	<1	0·5	>1	>1	*f*	>1

5. Discussion of Results

Crystal Structure and Normal Oscillations.—In order to interpret the foregoing results satisfactorily, it is necessary that a reference should be made to the complete analysis of the normal oscillations of the calcite and $NaNO_3$ lattices carried out by the author in an earlier paper.[1] The character table given below contains all the important features and applies to both $CaCO_3$ and $NaNO_3$.

TABLE III

D^6_{3d}	E	$2S^{\frac{1}{2}}$	$2C^1$	i	$3\sigma_v$	$3C_2$	n_i	External		n_i'	Activity in Raman effect	Surviving tensor components
								T	L			
A_1	1	1	1	1	1	1	1	0	0	1	p	a_{zz}, $a_{xx}+a_{yy}$
A_2	1	1	1	1	−1	−1	3	0	2	1	f	..
B_1	1	−1	1	−1	1	−1	4	1	2	1	f	..
B_2	1	−1	1	−1	−1	1	2	0	1	1	f	..
E_1	2	1	−1	−2	0	0	6	1	3	2	f	..
E_2	2	−1	−1	2	0	0	4	0	2	2	p	$\{(a_{xz}, a_{yz})$ $(a_{xy}, a_{xx}-a_{yy})$
w_R	10	2	4	2	0	4						
$h_i\chi_i'$	30	0	0	−6	0	−12						

The surviving tensor components are deduced by the application of the usual selection rules, the details of which will be omitted here. The trigonal axis is taken as the z-direction while the x and y axes lie in the plane of symmetry. These axes are fixed in the crystal and must be distinguished from the system fixed in space and described earlier. It may be remarked here that only one Raman-active normal oscillation (1084) comes under the total symmetric class and this is characterised by the fact that the diagonal terms of the polarisability tensor alone survive. The only other class under which Raman-active oscillations appear is E_2. Under this category, there are two lattice oscillations (155 and 282) and two internal oscillations (709 and 1434). The surviving components are mainly the non-diagonal ones although a term involving $\alpha_{xx} - \alpha_{yy}$ is present. It is thus clear that the scattering moment should be of the *polarised type* in the case of the total symmetric internal oscillation (1084) only whereas the scattering moment in the case of all the other oscillations, lattice as well as internal, may be a mixture of the *polarised* and the *depolarised* types. In addition to the selection rules cited above, we have also to consider the possibility of the various tensor components that appear in each case being unequal amongst themselves such as $\alpha_{xx} = \alpha_{yy} \neq \alpha_{zz}$. That such an inequality prominently exists is in fact clearly suggested by the result already noted in the foregoing section where it was observed that the change of polarisability of the CO_3 ion due to its total symmetric oscillation is much smaller when the incident light vector is perpendicular to the plane of the ion than when it is parallel to it. It may further be noted that the degree of such an anisotropy may be different for different normal oscillations. The combined effect of these two major factors, namely the selection rules and the anisotropy of the polarisation tensor will determine the ultimate characters of the Raman lines corresponding to each one of the normal oscillations. We may now deal with the various oscillations of the calcite lattice individually in the light of the above analysis.

Total Symmetric Oscillation (1084).—The set of equations (1) will determine the intensities of the various components in any general case.

$$\begin{aligned} p_x &= \alpha_{xx} E_x + \alpha_{xy} E_x + \alpha_{xz} E_z \\ p_y &= \alpha_{yx} E_x + \alpha_{yy} E_y + \alpha_{yz} E_z \\ p_z &= \alpha_{zx} E_x + \alpha_{zy} E_y + \alpha_{zz} E_{zz} \end{aligned} \qquad (1)$$

The p's and the E's stand for the components of the induced moment and of the incident light vector respectively. In the case of the 1084 line, we have all $\alpha_{ik} = 0$ and we shall postulate that α_{xx} which is equal to α_{yy} to be about three times as large as α_{zz}. Intensities involving α_{xx} or α_{yy} will accordingly be about ten times as large as those involving α_{zz}. The results that are to be

expected may be easily calculated and these are compared below in Table IV with the observations.

TABLE IV

Serial Number	Component in the incident light	Components in the scattered light		Intensities calculated (1084) OX	OZ	Intensities observed (1084) OX	OZ
1	E_x	p_z	p_x	0	100	5	200
2	E_y	p_z	p_x	0	0	2	5
3	E_x	p_y	p_x	0	100	60	100
4	E_z	p_y	p_x	0	0	20	10
5	E_z	p_x	p_z	0	10	5	10
6	E_y	p_x	p_z	0	0	50	5

Numbers in column 1 of Table IV correspond to the numbers in column 1 of Table I. The x, y and z occurring in columns 2 and 3 of Table IV refer to the system of axes in which the z-direction is always identified with the trigonal axis of the crystal. OX and OZ occurring in columns 4 and 5 have the significance given to them earlier and refer to the space fixed co-ordinate system. With the exception of the unusually large OX intensities observed in cases 3 and 6, the experimental results may be regarded as being in excellent agreement with the theoretical expectations. A close examination of cases 3 and 6 however shows that the circumstances are particularly favourable for the presence of the proper component in the incident light due to convergence which will account for such abnormally large OX intensities.

Lattice Oscillations (155 and 282).—In this case, equations (1) still hold good but we have $\alpha_{xz} = 0$. We will also assume that α_{xy}, α_{xx} and α_{yy} are comparatively small and that α_{xy} and α_{yz} are both large and approximately equal. The expected results are shown in Table V along with observed figures.

TABLE V

Serial Number	Component in the incident light	Components in the scattered light		Intensities calculated OX	OZ	Intensities observed (155) OX	OZ	Intensities observed (282 OX	OZ
1	E_x	p_z	p_x	large	..	25	1	60	2
2	E_y	p_z	p_x	large		50	..	100	..
3	E_x	p_y	p_x	..	..	5	5	10	10
4	E_z	p_y	p_x	large	large	50	50	100	100
5	E_z	p_x	p_z	large	0	50	0	100	3
6	E_y	p_x	p_z	..	large	25	50	50	100

Notation in Table V is the same as that adopted in Table IV. Agreement between the observed and the calculated characters is very satisfactory. It must be remarked here that both the lattice oscillations have been treated exactly alike both in respect of the selection rules and the degree of anisotropy of the polarisation tensor. The latter is only an assumption which is justified by the results whereas the former is a consequence of the fact that both of them come under the same irreducible representation.

Internal Degenerate Oscillations (709 *and* 1434).—These two oscillations also come under the irreducible representrion E_z and the selection rules are therefore the same as those that have been found to hold good for the lattice lines. It is however known that in these oscillations, the movements of the atoms are confined to the plane of the CO_3 group only (see Ref. 1) and further special considerations will therefore apply. It is easily seen that in such oscillations, the symmetry axis remains as one of the principal directions (z-direction) of the polarisability tensor during the oscillation while the x and y axes may change but being confined to the plane of symmetry only. This means that $\alpha_{xz} = \alpha_{yz} = 0$ and an incident light vector in which the vibrations are confined to the symmetry plane will give rise to an induced moment which is also confined to the symmetry plane. In this respect, their behaviour is akin to that of the total symmetric oscillation and reciprocal of that exhibited by the lattice lines. It may however be noted that an incident light vector which is perpendicular to the plane of the group will not give rise to any induced moment at all since α_{zz} is also equal to zero. This is in conformity with the failure to record these lines in the plate corresponding to number 5 of Table I. A more detailed correlation will not be attempted as these lines are inherently weak and their components have not been recorded in all cases.

First Overtone of the Raman Inactive Oscillation (1749).—There is a fundamental frequency at 879 arising from a non-degenerate oscillation of the lattice which is Raman inactive. The overtone in question refers to this and will accordingly be put under the total symmetric class.† It should therefore exhibit characters which are more or less similar to those exhibited by the 1084 itself. This expectation is supported by the meagre experimental results that are obtained in the present investigation.

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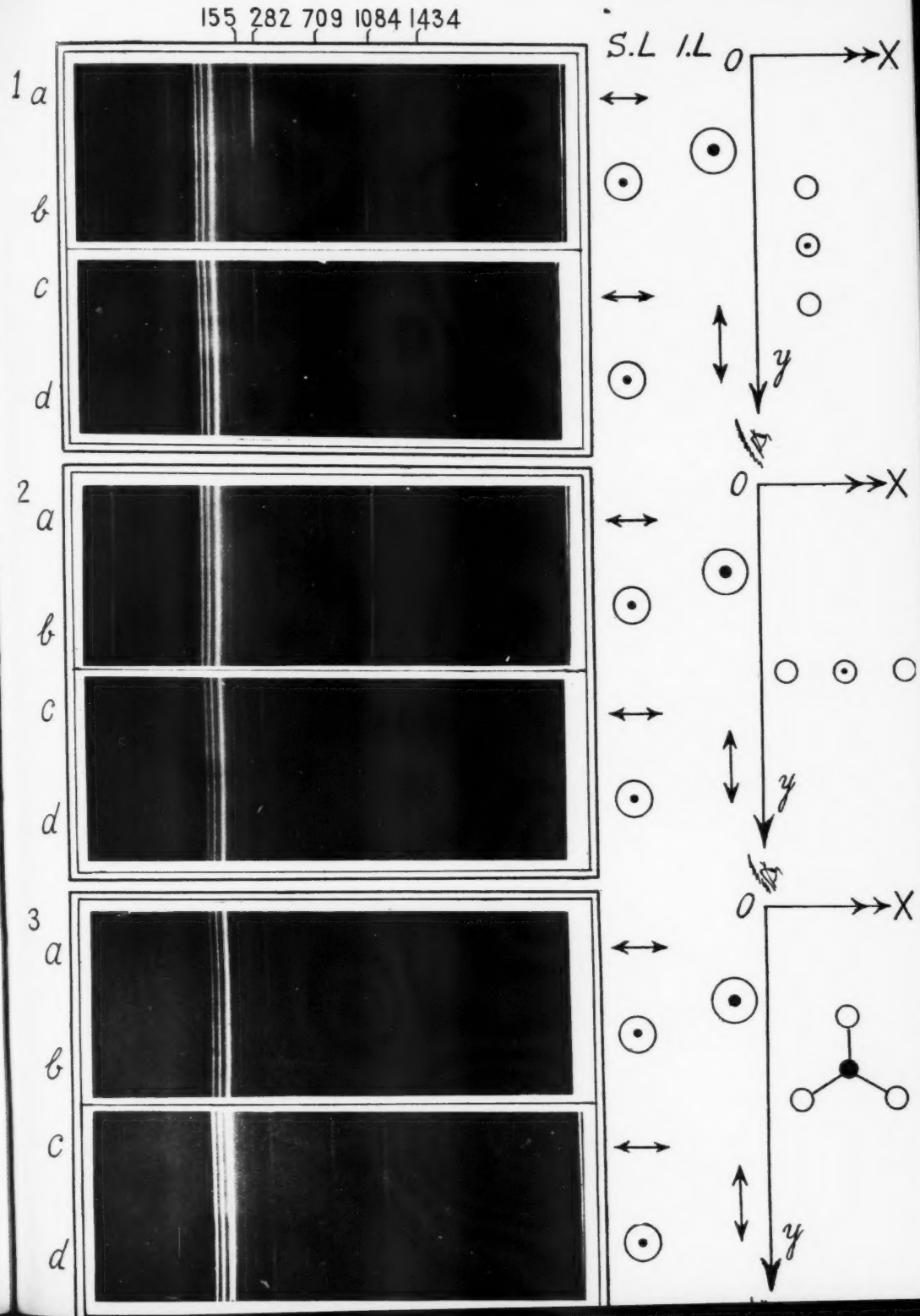
† See reference 1 where it was shown that the representation of the overtones of all non-degenerate irreducible representations is equivalent to the irreducible representation of the total symmetric type.


155 282 709 1084 1434
S.L I.L
O
X
y
1 a
b
c
d
2 a
b
c
d
3 a
b
c
d

6. Summary

The results of studying the Raman effect in a specially cut and polished single crystal of calcite are reported in the paper. Twelve spectrograms corresponding to different orientations of the crystal with respect to the directions of incidence and observation are obtained. The most important result of the investigation is the reciprocal behaviour of the lattice oscillations on the one hand and the total symmetric oscillation on the other. This is to be expected theoretically as the former belong to a degenerate class whereas the latter comes under an altogether different representation possessing special features. Two other degenerate internal frequencies which are Raman-active resemble the total symmetric oscillation in many important respects. The first overtone of a Raman inactive fundamental is recorded in two spectra and in these cases, it is found to resemble the total symmetric oscillation. The results of this paper are in general agreement with those already reported by Nedungadi who worked with the closely analogous case of $NaNO_3$.

An attempt is made to explain the observed results by studying the selection rules in detail. The peculiar features of the recorded spectrograms indicate that the strong optical birefringence of the crystal which would naturally manifest itself in Rayleigh scattering has its parallel when we come to consider the Raman scattering. The polarisation tensor associated with each vibrational transition should accordingly be regarded as anisotropic and the type of anisotropy or the degree of anisotropy may vary from one normal vibration to another. This fact combined with the selection rules provides satisfactory explanation for most of the observed results. Small discrepancies which still remain unexplained may be attributed to errors arising from the convergence of the incident beam.

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3·40 Printed at The Bangalore Press, Bangalore City, by G. Srinivasa Rao, Superintendent,
and Published by The Idian Academy of Sciences, Bangalore